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Vol. 34. No. 297. September 1948.

CALIBRATION OF CYLINDRICAL TANKS WITH AXIS INCLINED.

By W. L. Coats * (Associate Fellow).

The method described in this paper provides a means for calculating the partial volumes of cylindrical tanks at any angle of slope, in a manner more or less the same as for horizontal tanks. The method is mathematically exact, but is not applicable to tanks which are truly horizontal.

For truly horizontal tanks as well as for tilted horizontal tanks, a method of calibration was proposed some years ago by Dr. Alfred Basch, chief gauger of the Federal Office for Gauging and Measuring, Vienna (Petrol. Z., 1937, **33**, (3), 1–8), *but because close approximations to true volumes are obtained at reasonably small angles of tilt only, the Basch method cannot be universally applied. For cylinders which are substantially tilted the method in this paper has clear advantages.*

The Tank Calibration Panel of the Institute's Standardization Sub-Committee No. 1 is currently giving close attention to the production of standardized procedures for calibrating horizontal oil containers. Both the Coats and the Basch methods will undoubtedly receive their close attention.

In the meantime the Panel would welcome comments on Mr. Coats's paper as well as views on the general question of horizontal tank calibration.

H. Hyams,
Chairman, I.P. Oil Measurement
and Sampling Sub-Committee.

The method about to be described enables the calibration of cylindrical tanks lying at any angle of slope to be calculated in more or less the same manner as for horizontal tanks and with the same degree of accuracy. Moreover, the extra work involved is not great.

General.

Referring to Fig. 1, $ABEF$ is a cylindrical tank, length L, diameter D, with axis inclined to the horizontal at an angle θ and filled with liquid up to the level HJ.

Fig. 2 represents a cross-section of the cylinder at any plane such as X–X normal to the axis, this cross-section being intersected by the plane HJ at LL. The height LM in Fig. 1 or PM in Fig. 2 is denoted by h and the angle which the radius OL makes with the vertical by ϕ. At the left hand end of the cylinder ϕ has the definite value ϕ_1 and at the right hand end of the cylinder the definite value ϕ_2.

If the cross-sectional area of the lower section of the cylinder at the plane of intersection X–X, that is, the area of the segment LML, be denoted by a, then the volume of the section of the cylinder which lies below the plane of intersection HJ is given by,

$$V = \int_0^L a \times dL \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* Shell-Mex & B.P. Ltd. Deputy Chairman, Tank Calibration Panel, Standardization Sub-Committee No. 1 (Measurement and Sampling).

Expressing a and dL in terms of ϕ, we have

$$V = \int_{\phi_2}^{\phi_1} r^2(\phi - \sin\phi\cos\phi)\frac{r}{\tan\theta}\sin\phi \times d\phi$$

which reduces to

$$V = \frac{r^3}{\tan\theta}\left[\int_{\phi_2}^{\phi_1} \sin\phi\,(1 - \tfrac{1}{3}\sin^2\phi) - \phi\cos\phi\right] \quad . \quad . \quad (2)$$

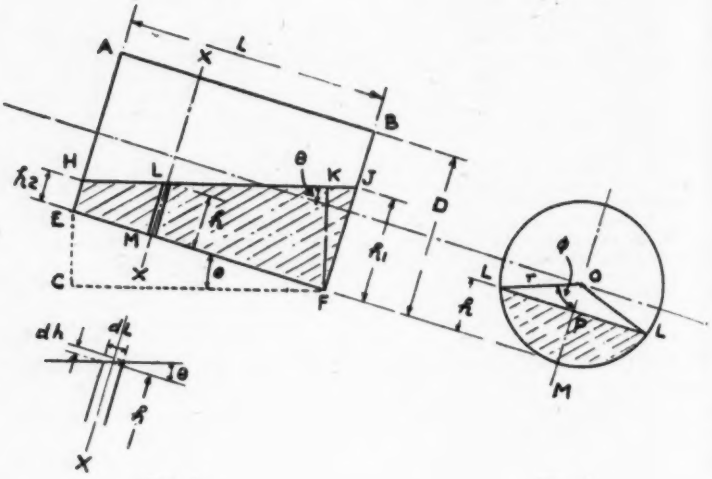

FIG. 1.

FIG. 2.

If the value of the function inside the bracket corresponding to ϕ_1 be q_1, and the value corresponding to ϕ_2 be q_2, we have

$$V = \frac{r^3}{\tan\theta}[q_1 - q_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is obvious that q_1 and q_2 are functions purely of ϕ_1 and ϕ_2 respectively. In other words they are governed entirely by the level of the liquid at the low and high ends of the tank respectively; or, to be more precise, by the ratio of the height of the liquid to tank diameter at these two points, namely $\frac{h_1}{D}$ and $\frac{h_2}{D}$. For convenience these two ratios will be denoted by m_1 and m_2.

If, therefore, we had a table of values of q, based on m as argument, it would suffice for all calculations, irrespective of the dimensions or angle of slope of the tank. The latter are taken care of by r^3 and tan θ.

The evaluation of q by means of equation (3) is rather a formidable task and prompted the search for an easier method.

The total capacity of the cylinder is $C = \pi r^2 L$.

Hence, $$r^2 = \frac{C}{\pi L}; \quad \text{and } r^3 = \frac{C}{\pi L} \times \frac{D}{2}$$

so that,

$$\frac{r^3}{\tan\theta} = \frac{C}{\pi L} \times \frac{D}{2\tan\theta} = C \times \frac{D}{L\tan\theta} \times \frac{1}{2\pi} = \frac{C}{s} \times \frac{1}{2\pi};$$

where $s = \frac{L}{D}\tan\theta$.

Equation (3) can therefore be rewritten

$$V = \frac{C}{s}\left[\frac{q_1}{2\pi} - \frac{q_2}{2\pi}\right]$$

or $$\frac{C}{s}(p_1 - p_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Reverting to equation (1) this can also be expressed as

$$V = \Sigma a \times dL \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

thereby visualizing the volume as the summation of a series of thin slices, parallel to XX, each of thickness dL.

Using the substitution $dL = \frac{dh}{\tan\theta}$ and multiplying numerator and denominator by $2\pi r^3$, equation (5) can be written

$$V = \frac{C}{s}\Sigma\frac{a}{\pi r^2} \times \frac{dh}{D} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Assume HJ produced to cut the base line produced in V, and the upper edge, produced, in Z, as in Fig. 3, and consider the cylinder extended to WV and ZY.

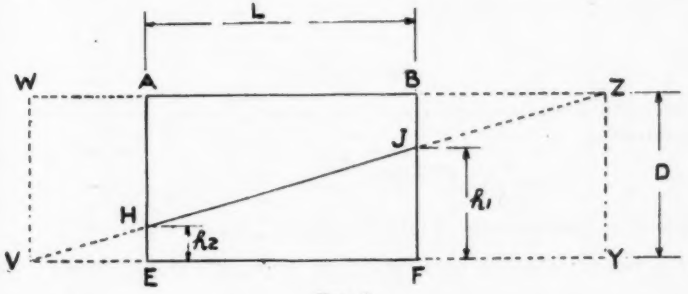

FIG. 3.

$\frac{C}{s}$ is the volume of the extended cylinder $WVZY$ and $\Sigma\frac{a}{\pi r^2} \times \frac{dh}{D}$ the volume of any cylindrical ungula such as VJF, expressed as a fraction of the volume of that cylinder. If this ratio be denoted by p_1 in the case of

the ungula VJF and by p_2 in the case of the ungula VHE, the volume of the truncated ungula $HEJF$ will be

$$V = \frac{C}{s}(p_1 - p_2)$$

This is identical with equation (4), hence it is obvious that the required values of p can be obtained from the expression

$$\Sigma \frac{a}{\pi r^2} \times \frac{dh}{D}$$

$\frac{a}{\pi r^2}$ is the ratio of a cross-sectional area of the ungula (in this case a segment of a circle) to the area of the whole circle and $\frac{dh}{D}$ is the increment in height of successive segments expressed as a fraction of the diameter of a circle.

Tables are available giving the areas of segments of a circle expressed as fractions of the whole circle, to the seventh decimal place and at intervals of 0·001 of the diameter. Summing these segmental areas from zero upwards gave a complete range of values of p expressed to the tenth decimal place. These values, entered against the argument m and rounded off to the ninth decimal place, are given in Table I. The need for this degree of accuracy is explained later.

It was not necessary, of course, to make a complete summation for each individual value of p. Starting off with the lowest value, subsequent values were built up by successive additions thereto. Finally, having obtained all the values from zero up to half the diameter of the cylinder, the remaining values were derived from them by means of a simple relationship which exists between the two.

Incidentally there is a simple relationship between m_1 and m_2.

Referring again to Fig. 1, it will be seen that $h_1 - h_2 = L \tan \theta$; so that $\frac{h_1}{D} - \frac{h_2}{D} = \frac{L}{D} \tan \theta$; that is, $m_1 - m_2 = s$; or, $m_2 = m_1 - s$.

Application.

Recapitulating, the capacity of the tank up to any level is given by the formula

$$\text{Gallons} = \frac{C}{s}(p_1 - p_2)$$

where C = total capacity of tank in gallons

$s = \frac{L}{D} \tan \theta$. This has been termed the slope ratio and is a constant for any one tank and angle of slope.

p_1 and p_2 are coefficients of capacity, the values of which appropriate to any particular value of m are obtained from Table I.

To obtain m_1 (and hence also m_2) it is first necessary to adjust all dip readings to give the corresponding reading at the lower corner of the

TABLE I.

Values of Capacity Coefficient p.

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·000	0·0000000 00			0·050	0·0003755 11		
		22				189 71	554
0·001	0·0000000 22		78	0·051	0·0003944 82		561
		1 00				195 32	
0·002	0·0000001 22		113	0·052	0·0004140 14		565
		2 13				200 97	
0·003	0·0000003 35		139	0·053	0·0004341 11		570
		3 52				206 67	
0·004	0·0000006 87		160	0·054	0·0004547 78		576
		5 12				212 43	
0·005	0·0000011 99		180	0·055	0·0004760 21		581
		6 92				218 24	
0·006	0·0000018 91		197	0·056	0·0004978 45		585
		8 89				224 09	
0·007	0·0000027 80		212	0·057	0·0005202 54		590
		11 01				229 99	
0·008	0·0000038 81		226	0·058	0·0005432 53		596
		13 27				235 95	
0·009	0·0000052 08		241	0·059	0·0005668 48		600
		15 68				241 95	
0·010	0·0000067 76		253	0·060	0·0005910 43		604
		18 21				247 99	
0·011	0·0000085 97		266	0·061	0·0006158 42		610
		20 87				254 09	
0·012	0·0000106 84		277	0·062	0·0006412 51		614
		23 64				260 23	
0·013	0·0000130 48		289	0·063	0·0006672 74		619
		26 53				266 42	
0·014	0·0000157 01		299	0·064	0·0006939 16		623
		29 52				272 65	
0·015	0·0000186 53		309	0·065	0·0007211 81		627
		32 61				278 92	
0·016	0·0000219 14		319	0·066	0·0007490 73		633
		35 80				285 25	
0·017	0·0000254 94		330	0·067	0·0007775 98		637
		39 10				291 62	
0·018	0·0000294 04		339	0·068	0·0008067 60		641
		42 49				298 03	
0·019	0·0000336 53		347	0·069	0·0008365 63		645
		45 96				304 48	
0·020	0·0000382 49		356	0·070	0·0008670 11		649
		49 52				310 97	
0·021	0·0000432 01		366	0·071	0·0008981 08		655
		53 18				317 52	
0·022	0·0000485 19		373	0·072	0·0009298 60		658
		56 91				324 10	
0·023	0·0000542 10		382	0·073	0·0009622 70		663
		60 73				330 73	
0·024	0·0000602 83		389	0·074	0·0009953 43		666
		64 62				337 39	
0·025	0·0000667 45		398	0·075	0·0010290 82		670
		68 60				344 09	
0·026	0·0000736 05		405	0·076	0·0010634 91		676
		72 65				350 85	
0·027	0·0000808 70		413	0·077	0·0010985 76		679
		76 78				357 64	
0·028	0·0000885 48		420	0·078	0·0011343 40		682
		80 98				364 46	
0·029	0·0000966 46		428	0·079	0·0011707 86		687
		85 26				371 33	
0·030	0·0001051 72		434	0·080	0·0012079 19		691
		89 60				378 24	
0·031	0·0001141 32		441	0·081	0·0012457 43		695
		94 01				385 19	
0·032	0·0001235 33		448	0·082	0·0012842 62		698
		98 49				392 17	
0·033	0·0001333 82		455	0·083	0·0013234 79		703
		103 04				399 20	
0·034	0·0001436 86		462	0·084	0·0013633 99		706
		107 66				406 26	
0·035	0·0001544 52		468	0·085	0·0014040 25		711
		112 34				413 37	
0·036	0·0001656 86		474	0·086	0·0014453 62		714
		117 08				420 51	
0·037	0·0001773 94		480	0·087	0·0014874 13		717
		121 88				427 68	
0·038	0·0001895 82		488	0·088	0·0015301 81		721
		126 76				434 89	
0·039	0·0002022 58		493	0·089	0·0015736 70		726
		131 69				442 15	
0·040	0·0002154 27		499	0·090	0·0016178 85		728
		136 68				449 43	
0·041	0·0002290 95		504	0·091	0·0016628 28		733
		141 72				456 76	
0·042	0·0002432 67		511	0·092	0·0017085 04		736
		146 83				464 12	
0·043	0·0002579 50		517	0·093	0·0017549 16		739
		152 00				471 51	
0·044	0·0002731 50		522	0·094	0·0018020 67		744
		157 22				478 95	
0·045	0·0002888 72		528	0·095	0·0018499 62		746
		162 50				486 41	
0·046	0·0003051 22		533	0·096	0·0018986 03		750
		167 83				493 91	
0·047	0·0003219 05		539	0·097	0·0019479 94		754
		173 22				501 45	
0·048	0·0003392 27		545	0·098	0·0019981 39		757
		178 67				509 02	
0·049	0·0003570 94		550	0·099	0·0020490 41		761
		184 17				516 63	

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·100	0·0021007 04			0·150	0·0057231 13		
		524 27	764			945 15	909
0·101	0·0021531 31	531 94	767	0·151	0·0058176 28	954 27	912
0·102	0·0022063 25	539 64	770	0·152	0·0059130 55	963 41	914
0·103	0·0022602 89	547 39	775	0·153	0·0060093 96	972 58	917
0·104	0·0023150 28	555 16	777	0·154	0·0061066 54	981 77	919
0·105	0·0023705 44	562 96	780	0·155	0·0062048 31	990 99	922
0·106	0·0024268 40	570 80	784	0·156	0·0063039 30	1000 23	924
0·107	0·0024839 20	578 68	788	0·157	0·0064039 53	1009 49	926
0·108	0·0025417 88	586 58	790	0·158	0·0065049 02	1018 78	929
0·109	0·0026004 46	594 52	794	0·159	0·0066067 80	1028 09	931
0·110	0·0026598 98		796	0·160	0·0067095 89		933
		602 48				1037 42	
0·111	0·0027201 46	610 48	800	0·161	0·0068133 31	1046 79	937
0·112	0·0027811 94	618 51	803	0·162	0·0069180 10	1056 17	938
0·113	0·0028430 45	626 58	807	0·163	0·0070236 27	1065 58	941
0·114	0·0029057 03	634 67	809	0·164	0·0071301 85	1075 00	942
0·115	0·0029691 70	642 79	812	0·165	0·0072376 85	1084 45	945
0·116	0·0030334 49	650 95	816	0·166	0·0073461 30	1093 93	948
0·117	0·0030985 44	659 13	818	0·167	0·0074555 23	1103 43	950
0·118	0·0031644 57	667 35	822	0·168	0·0075658 66	1112 95	952
0·119	0·0032311 92	675 59	824	0·169	0·0076771 61	1122 49	954
0·120	0·0032987 51		827	0·170	0·0077894 10		957
		683 86				1132 06	
0·121	0·0033671 37	692 17	831	0·171	0·0079026 16	1141 64	958
0·122	0·0034363 54	700 51	834	0·172	0·0080167 80	1151 25	961
0·123	0·0035064 05	708 87	836	0·173	0·0081319 05	1160 89	964
0·124	0·0035772 92	717 26	839	0·174	0·0082479 94	1170 54	965
0·125	0·0036490 18	725 68	842	0·175	0·0083650 48	1180 22	968
0·126	0·0037215 86	734 14	846	0·176	0·0084830 70	1189 91	969
0·127	0·0037950 00	742 62	848	0·177	0·0086020 61	1199 63	972
0·128	0·0038692 62	751 12	850	0·178	0·0087220 24	1209 37	974
0·129	0·0039443 74	759 65	853	0·179	0·0088429 61	1219 14	977
0·130	0·0040203 39		857	0·180	0·0089648 75		978
		768 22				1228 92	
0·131	0·0040971 61	776 81	859	0·181	0·0090877 67	1238 72	980
0·132	0·0041748 42	785 44	863	0·182	0·0092166 39	1248 55	983
0·133	0·0042533 86	794 08	864	0·183	0·0093364 94	1258 39	984
0·134	0·0043327 94	802 75	867	0·184	0·0094623 33	1268 26	987
0·135	0·0044130 69	811 46	871	0·185	0·0095891 59	1278 15	989
0·136	0·0044942 15	820 18	872	0·186	0·0097169 74	1288 06	991
0·137	0·0045762 33	828 94	876	0·187	0·0098457 80	1297 99	993
0·138	0·0046591 27	837 72	878	0·188	0·0099755 79	1307 93	994
0·139	0·0047428 99	846 53	881	0·189	0·0101063 90	1317 90	997
0·140	0·0048275 52		884	0·190	0·0102381 62		1000
		855 37				1327 90	
0·141	0·0049130 89	864 23	886	0·191	0·0103709 52	1337 91	1001
0·142	0·0049995 12	873 12	889	0·192	0·0105047 43	1347 94	1003
0·143	0·0050868 24	882 04	892	0·193	0·0106395 37	1357 98	1004
0·144	0·0051750 28	890 97	893	0·194	0·0107753 35	1368 05	1007
0·145	0·0052641 25	899 94	897	0·195	0·0109121 40	1378 15	1010
0·146	0·0053541 19	908 94	900	0·196	0·0110499 55	1388 25	1010
0·147	0·0054450 13	917 95	901	0·197	0·0111887 80	1398 38	1013
0·148	0·0055368 08	926 99	904	0·198	0·0113286 18	1408 53	1015
0·149	0·0056295 07	936 06	907	0·199	0·0114694 71	1418 70	1017

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·200	0·0116113 41		1018	0·250	0·0200408 35		1103
		1428 88				1960 53	
0·201	0·0117542 29		1020	0·251	0·0202368 88		1104
		1439 08				1971 57	
0·202	0·0118981 37		1023	0·252	0·0204340 45		1105
		1449 31				1982 62	
0·203	0·0120430 68		1025	0·253	0·0206323 07		1107
		1459 56				1993 69	
0·204	0·0121890 24		1025	0·254	0·0208316 76		1109
		1469 81				2004 78	
0·205	0·0123360 05		1028	0·255	0·0210321 54		1110
		1480 09				2015 88	
0·206	0·0124840 14		1031	0·256	0·0212337 42		1111
		1490 40				2026 99	
0·207	0·0126330 54		1031	0·257	0·0214364 41		1113
		1500 71				2038 12	
0·208	0·0127831 25		1033	0·258	0·0216402 53		1114
		1511 04				2049 26	
0·209	0·0129342 29		1036	0·259	0·0218451 79		1116
		1521 40				2060 42	
0·210	0·0130863 69		1037	0·260	0·0220512 21		1116
		1531 77				2071 58	
0·211	0·0132395 46		1040	0·261	0·0222583 79		1119
		1542 17				2082 77	
0·212	0·0133937 63		1040	0·262	0·0224666 56		1120
		1552 57				2093 97	
0·213	0·0135490 20		1042	0·263	0·0226760 53		1121
		1562 99				2105 18	
0·214	0·0137053 19		1045	0·264	0·0228865 71		1122
		1573 44				2116 40	
0·215	0·0138626 63		1046	0·265	0·0230982 11		1124
		1583 90				2127 64	
0·216	0·0140210 53		1048	0·266	0·0233109 75		1126
		1594 38				2138 90	
0·217	0·0141804 91		1050	0·267	0·0235248 65		1126
		1604 88				2150 16	
0·218	0·0143409 79		1051	0·268	0·0237398 81		1128
		1615 39				2161 44	
0·219	0·0145025 18		1053	0·269	0·0239560 25		1129
		1625 92				2172 73	
0·220	0·0146651 10		1055	0·270	0·0241732 98		1131
		1636 47				2184 04	
0·221	0·0148287 57		1057	0·271	0·0243917 02		1131
		1647 04				2195 35	
0·222	0·0149934 61		1058	0·272	0·0246112 37		1133
		1657 62				2206 68	
0·223	0·0151592 23		1060	0·273	0·0248319 05		1135
		1668 22				2218 03	
0·224	0·0153260 45		1062	0·274	0·0250537 08		1136
		1678 84				2229 39	
0·225	0·0154939 29		1063	0·275	0·0252766 47		1137
		1689 47				2240 76	
0·226	0·0156628 76		1065	0·276	0·0255007 23		1138
		1700 12				2252 14	
0·227	0·0158328 88		1067	0·277	0·0257259 37		1140
		1710 79				2263 54	
0·228	0·0160039 67		1068	0·278	0·0259522 91		1140
		1721 47				2274 94	
0·229	0·0161761 14		1070	0·279	0·0261797 85		1143
		1732 17				2286 37	
0·230	0·0163493 31		1072	0·280	0·0264084 22		1143
		1742 89				2297 80	
0·231	0·0165236 20		1073	0·281	0·0266382 02		1145
		1753 62				2309 25	
0·232	0·0166989 82		1075	0·282	0·0268691 27		1145
		1764 37				2320 70	
0·233	0·0168754 19		1076	0·283	0·0271011 97		1147
		1775 13				2332 17	
0·234	0·0170529 32		1079	0·284	0·0273344 14		1149
		1785 92				2343 66	
0·235	0·0172315 24		1079	0·285	0·0275687 80		1150
		1796 71				2355 16	
0·236	0·0174111 95		1081	0·286	0·0278042 96		1150
		1807 52				2366 66	
0·237	0·0175919 47		1084	0·287	0·0280409 62		1152
		1818 36				2378 18	
0·238	0·0177737 83		1084	0·288	0·0282787 80		1153
		1829 20				2389 71	
0·239	0·0179567 03		1085	0·289	0·0285177 51		1155
		1840 05				2401 26	
0·240	0·0181407 08		1088	0·290	0·0287578 77		1155
		1850 93				2412 81	
0·241	0·0183258 01		1090	0·291	0·0289991 58		1156
		1861 83				2424 37	
0·242	0·0185119 84		1091	0·292	0·0292415 95		1158
		1872 74				2435 95	
0·243	0·0186992 58		1091	0·293	0·0294851 90		1160
		1883 65				2447 55	
0·244	0·0188876 23		1094	0·294	0·0297299 45		1160
		1894 59				2459 15	
0·245	0·0190770 82		1095	0·295	0·0299758 60		1161
		1905 54				2470 76	
0·246	0·0192676 36		1097	0·296	0·0302229 36		1162
		1916 51				2482 38	
0·247	0·0194592 87		1098	0·297	0·0304711 74		1164
		1927 49				2494 02	
0·248	0·0196520 36		1100	0·298	0·0307205 76		1165
		1938 49				2505 67	
0·249	0·0198458 85		1101	0·299	0·0309711 43		1165
		1949 50				2517 32	

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·300	0·0312228 75			0·350	0·0453188 20		
		2528 99	1167			3125 26	1215
0·301	0·0314757 74		1169	0·351	0·0456313 46		1216
		2540 68				3137 42	
0·302	0·0317298 42		1169	0·352	0·0459450 88		1216
		2552 37				3149 58	
0·303	0·0319850 79		1170	0·353	0·0462600 46		1217
		2564 07				3161 75	
0·304	0·0322414 86		1171	0·354	0·0465762 21		1217
		2575 78				3173 92	
0·305	0·0324990 64		1173	0·355	0·0468936 13		1219
		2587 51				3186 11	
0·306	0·0327578 15		1173	0·356	0·0472122 24		1219
		2599 24				3198 30	
0·307	0·0330177 39		1175	0·357	0·0475320 54		1221
		2610 99				3210 51	
0·308	0·0332788 38		1175	0·358	0·0478531 05		1220
		2622 74				3222 71	
0·309	0·0335411 12		1177	0·359	0·0481753 76		1222
		2634 51				3234 93	
0·310	0·0338045 63			0·360	0·0484988 69		1222
		2646 29	1178			3247 15	
0·311	0·0340691 92		1179	0·361	0·0488235 84		1223
		2658 08				3259 38	
0·312	0·0343350 00		1179	0·362	0·0491495 22		1224
		2669 87				3271 62	
0·313	0·0346019 87		1181	0·363	0·0494766 84		1224
		2681 68				3283 86	
0·314	0·0348701 55		1182	0·364	0·0498050 70		1226
		2693 50				3296 12	
0·315	0·0351395 05		1183	0·365	0·0501346 82		1226
		2705 33				3308 38	
0·316	0·0354100 38		1184	0·366	0·0504655 20		1226
		2717 17				3320 64	
0·317	0·0356817 55		1185	0·367	0·0507975 84		1227
		2729 02				3332 91	
0·318	0·0359546 57		1185	0·368	0·0511308 75		1229
		2740 87				3345 20	
0·319	0·0362287 44		1187	0·369	0·0514653 95		1229
		2752 74				3357 49	
0·320	0·0365040 18			0·370	0·0518011 44		1229
		2764 62	1188			3369 78	
0·321	0·0367804 80		1189	0·371	0·0521381 22		1230
		2776 51				3382 08	
0·322	0·0370581 31		1190	0·372	0·0524763 30		1231
		2788 41				3394 39	
0·323	0·0373369 72		1191	0·373	0·0528157 69		1231
		2800 32				3406 70	
0·324	0·0376170 04		1192	0·374	0·0531564 39		1233
		2812 24				3419 03	
0·325	0·0378982 28		1192	0·375	0·0534983 42		1232
		2824 16				3431 35	
0·326	0·0381806 44		1194	0·376	0·0538414 77		1234
		2836 10				3443 69	
0·327	0·0384642 54		1194	0·377	0·0541858 46		1234
		2848 04				3456 03	
0·328	0·0387490 58		1196	0·378	0·0545314 49		1234
		2860 00				3468 37	
0·329	0·0390350 58		1197	0·379	0·0548782 86		1236
		2871 97				3480 73	
0·330	0·0393222 55			0·380	0·0552263 59		1236
		2883 94	1197			3493 09	
0·331	0·0396106 49		1198	0·381	0·0555756 68		1237
		2895 92				3505 46	
0·332	0·0399002 41		1199	0·382	0·0559262 14		1237
		2907 91				3517 83	
0·333	0·0401910 32		1200	0·383	0·0562779 97		1238
		2919 91				3530 21	
0·334	0·0404830 23		1202	0·384	0·0566310 18		1239
		2931 93				3542 60	
0·335	0·0407762 16		1202	0·385	0·0569852 78		1238
		2943 95				3554 98	
0·336	0·0410706 11		1202	0·386	0·0573407 76		1240
		2955 97				3567 38	
0·337	0·0413662 08		1204	0·387	0·0576975 14		1241
		2968 01				3579 79	
0·338	0·0416630 09		1205	0·388	0·0580554 93		1240
		2980 06				3592 19	
0·339	0·0419610 15		1205	0·389	0·0584147 12		1242
		2992 11				3604 61	
0·340	0·0422602 26			0·390	0·0587751 73		1242
		3004 17	1206			3617 03	
0·341	0·0425606 43		1207	0·391	0·0591368 76		1243
		3016 24				3629 46	
0·342	0·0428622 67		1208	0·392	0·0594998 22		1243
		3028 32				3641 89	
0·343	0·0431650 99		1209	0·393	0·0598640 11		1243
		3040 41				3654 32	
0·344	0·0434691 40		1210	0·394	0·0602294 43		1245
		3052 51				3666 77	
0·345	0·0437743 91		1211	0·395	0·0605961 20		1244
		3064 62				3679 21	
0·346	0·0440808 53		1211	0·396	0·0609640 41		1246
		3076 73				3691 67	
0·347	0·0443885 26		1212	0·397	0·0613332 08		1246
		3088 85				3704 13	
0·348	0·0446974 11		1213	0·398	0·0617036 21		1247
		3100 98				3716 60	
0·349	0·0450075 09		1213	0·399	0·0620752 81		1246
		3113 11				3729 06	

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·400	0·0624481 87			0·450	0·0826935 18		
		3741 54	1248			4370 77	1266
0·401	0·0628223 41		1248	0·451	0·0831305 95		1268
		3754 02				4383 45	
0·402	0·0631977 43		1248	0·452	0·0835689 40		1267
		3766 50				4396 12	
0·403	0·0635743 93		1250	0·453	0·0840085 52		1268
		3779 00				4408 80	
0·404	0·0639522 93		1249	0·454	0·0844494 32		1268
		3791 49				4421 48	
0·405	0·0643314 42		1250	0·455	0·0848915 80		1268
		3803 99				4434 16	
0·406	0·0647118 41		1251	0·456	0·0853349 96		1268
		3816 50				4446 84	
0·407	0·0650934 91		1250	0·457	0·0857796 80		1269
		3829 00				4459 53	
0·408	0·0654763 91		1252	0·458	0·0862256 33		1268
		3841 52				4472 21	
0·409	0·0658605 43		1252	0·459	0·0866728 54		1269
		3854 04				4484 90	
0·410	0·0662459 47		1253	0·460	0·0871213 44		1269
		3866 57				4497 59	
0·411	0·0666326 04		1253	0·461	0·0875711 03		1270
		3879 10				4510 29	
0·412	0·0670205 14		1253	0·462	0·0880221 32		1269
		3891 63				4522 98	
0·413	0·0674096 77		1253	0·463	0·0884744 30		1270
		3904 16				4535 68	
0·414	0·0678000 93		1255	0·464	0·0889279 98		1270
		3916 71				4548 38	
0·415	0·0681917 64		1255	0·465	0·0893828 36		1270
		3929 26				4561 08	
0·416	0·0685846 90		1255	0·466	0·0898389 44		1271
		3941 81				4573 79	
0·417	0·0689788 71		1255	0·467	0·0902963 23		1270
		3954 36				4586 49	
0·418	0·0693743 07		1256	0·468	0·0907549 72		1270
		3966 92				4599 19	
0·419	0·0697709 99		1257	0·469	0·0912148 91		1272
		3979 49				4611 91	
0·420	0·0701689 48		1257	0·470	0·0916760 82		1270
		3992 06				4624 61	
0·421	0·0705681 54		1257	0·471	0·0921385 43		1271
		4004 63				4637 32	
0·422	0·0709686 17		1257	0·472	0·0926022 75		1272
		4017 20				4650 04	
0·423	0·0713703 37		1258	0·473	0·0930672 79		1271
		4029 78				4662 75	
0·424	0·0717733 15		1259	0·474	0·0935335 54		1271
		4042 37				4675 46	
0·425	0·0721775 52		1259	0·475	0·0940011 00		1272
		4054 96				4688 18	
0·426	0·0725830 48		1259	0·476	0·0944699 18		1272
		4067 55				4700 90	
0·427	0·0729898 03		1260	0·477	0·0949400 08		1272
		4080 15				4713 62	
0·428	0·0733978 18		1260	0·478	0·0954113 70		1272
		4092 75				4726 34	
0·429	0·0738070 93		1260	0·479	0·0958840 04		1272
		4105 35				4739 06	
0·430	0·0742176 28		1261	0·480	0·0963579 10		1272
		4117 96				4751 78	
0·431	0·0746294 24		1260	0·481	0·0968330 88		1272
		4130 56				4764 50	
0·432	0·0750424 80		1262	0·482	0·0973095 38		1273
		4143 18				4777 23	
0·433	0·0754567 98		1262	0·483	0·0977872 61		1273
		4155 80				4789 96	
0·434	0·0758723 78		1262	0·484	0·0982662 57		1272
		4168 42				4802 68	
0·435	0·0762892 20		1262	0·485	0·0987465 25		1272
		4181 04				4815 40	
0·436	0·0767073 24		1263	0·486	0·0992280 65		1274
		4193 67				4828 14	
0·437	0·0771266 91		1264	0·487	0·0997108 79		1272
		4206 31				4840 86	
0·438	0·0775473 22		1263	0·488	0·1001949 65		1273
		4218 94				4853 59	
0·439	0·0779692 16		1263	0·489	0·1006803 24		1273
		4231 57				4866 32	
0·440	0·0783923 73		1264	0·490	0·1011669 56		1273
		4244 21				4879 05	
0·441	0·0788167 94		1265	0·491	0·1016548 61		1273
		4256 86				4891 78	
0·442	0·0792424 80		1265	0·492	0·1021440 39		1273
		4269 51				4904 51	
0·443	0·0796694 31		1264	0·493	0·1026344 90		1273
		4282 15				4917 24	
0·444	0·0800976 46		1265	0·494	0·1031262 14		1273
		4294 80				4929 97	
0·445	0·0805271 26		1266	0·495	0·1036192 11		1274
		4307 46				4942 71	
0·446	0·0809578 72		1266	0·496	0·1041134 82		1273
		4320 12				4955 44	
0·447	0·0813898 84		1266	0·497	0·1046090 26		1273
		4332 78				4968 17	
0·448	0·0818231 62		1267	0·498	0·1051058 43		1273
		4345 45				4980 90	
0·449	0·0822577 07		1266	0·499	0·1056039 33		1273
		4358 11				4993 63	

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·500	0·1061032 96			0·550	0·1326935 18		
		5006 37	1274			5641 89	1266
0·501	0·1066039 33			0·551	0·1332577 07		
		5019 10	1273			5654 55	1266
0·502	0·1071058 43			0·552	0·1338231 62		
		5031 83	1273			5667 22	1267
0·503	0·1076090 26			0·553	0·1343898 84		
		5044 56	1273			5679 88	1266
0·504	0·1081134 82			0·554	0·1349578 72		
		5057 29	1274			5692 54	1266
0·505	0·1086192 11			0·555	0·1355271 26		
		5070 03	1273			5705 20	1266
0·506	0·1091262 14			0·556	0·1360976 46		
		5082 76	1273			5717 85	1265
0·507	0·1096344 90			0·557	0·1366694 31		
		5095 49	1273			5730 49	1264
0·508	0·1101440 39			0·558	0·1372424 80		
		5108 22	1273			5743 14	1265
0·509	0·1106548 61			0·559	0·1378167 94		
		5120 95				5755 79	
0·510	0·1111669 56		1273	0·560	0·1383923 73		1264
		5133 68				5768 43	
0·511	0·1116803 24		1273	0·561	0·1389692 16		1263
		5146 41				5781 06	
0·512	0·1121949 65		1273	0·562	0·1395473 22		1263
		5159 14				5793 69	
0·513	0·1127108 79		1272	0·563	0·1401266 91		1264
		5171 86				5806 33	
0·514	0·1132280 65		1274	0·564	0·1407073 24		1263
		5184 60				5818 96	
0·515	0·1137465 25		1272	0·565	0·1412892 20		1262
		5197 32				5831 58	
0·516	0·1142662 57		1272	0·566	0·1418723 78		1262
		5210 04				5844 20	
0·517	0·1147872 61		1273	0·567	0·1424567 98		1262
		5222 77				5856 82	
0·518	0·1153095 38		1273	0·568	0·1430424 80		1262
		5235 50				5869 44	
0·519	0·1158330 88		1272	0·569	0·1436294 24		1260
		5248 22				5882 04	
0·520	0·1163579 10		1272	0·570	0·1442176 28		1261
		5260 94				5894 65	
0·521	0·1168840 04		1272	0·571	0·1448070 93		1260
		5273 66				5907 25	
0·522	0·1174113 70		1272	0·572	0·1453978 18		1260
		5286 38				5919 85	
0·523	0·1179400 08		1272	0·573	0·1459898 03		1260
		5299 10				5932 45	
0·524	0·1184699 18		1272	0·574	0·1465830 48		1259
		5311 82				5945 04	
0·525	0·1190011 00		1272	0·575	0·1471775 52		1259
		5324 54				5957 63	
0·526	0·1195335 54		1271	0·576	0·1477733 15		1259
		5337 25				5970 22	
0·527	0·1200672 79		1271	0·577	0·1483703 37		1258
		5349 96				5982 80	
0·528	0·1206022 75		1272	0·578	0·1489686 17		1257
		5362 68				5995 37	
0·529	0·1211385 43		1271	0·579	0·1495681 54		1257
		5375 39				6007 94	
0·530	0·1216760 82		1270	0·580	0·1501689 48		1257
		5388 09				6020 51	
0·531	0·1222148 91		1272	0·581	0·1507709 99		1257
		5400 81				6033 08	
0·532	0·1227549 72		1270	0·582	0·1513743 07		1256
		5413 51				6045 64	
0·533	0·1232963 23		1270	0·583	0·1519788 71		1255
		5426 21				6058 19	
0·534	0·1238389 44		1271	0·584	0·1525846 90		1255
		5438 92				6070 74	
0·535	0·1243828 36		1270	0·585	0·1531917 64		1255
		5451 62				6083 29	
0·536	0·1249279 98		1270	0·586	0·1538000 93		1255
		5464 32				6095 84	
0·537	0·1254744 30		1270	0·587	0·1544096 77		1253
		5477 02				6108 37	
0·538	0·1260221 32		1269	0·588	0·1550205 14		1253
		5489 71				6120 90	
0·539	0·1265711 03		1270	0·589	0·1556326 04		1253
		5502 41				6133 43	
0·540	0·1271213 44		1269	0·590	0·1562459 47		1253
		5515 10				6145 96	
0·541	0·1276728 54		1269	0·591	0·1568605 43		1252
		5527 79				6158 48	
0·542	0·1282256 33		1268	0·592	0·1574763 91		1252
		5540 47				6171 00	
0·543	0·1287796 80		1269	0·593	0·1580934 91		1250
		5553 16				6183 50	
0·544	0·1293349 96		1268	0·594	0·1587118 41		1251
		5565 84				6196 01	
0·545	0·1298915 80		1268	0·595	0·1593314 42		1250
		5578 52				6208 51	
0·546	0·1304494 32		1268	0·596	0·1599522 93		1249
		5591 20				6221 00	
0·547	0·1310085 52		1268	0·597	0·1605743 93		1250
		5603 88				6233 50	
0·548	0·1315689 40		1267	0·598	0·1611977 43		1248
		5616 55				6245 98	
0·549	0·1321305 95		1268	0·599	0·1618223 41		1248
		5629 23				6258 46	

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·600	0·1624481 87			0·650	0·1953188 20		
		6270 94	1248			6886 89	1215
0·601	0·1630752 81	6283 40	1246	0·651	0·1960075 09	6899 02	1213
0·602	0·1637036 21	6295 87	1247	0·652	0·1966974 11	6911 15	1213
0·603	0·1643332 08	6308 33	1246	0·653	0·1973885 26	6923 27	1212
0·604	0·1649640 41	6320 79	1246	0·654	0·1980808 53	6935 38	1211
0·605	0·1655961 20	6333 23	1244	0·655	0·1987743 91	6947 49	1211
0·606	0·1662294 43	6345 68	1245	0·656	0·1994691 40	6959 59	1210
0·607	0·1668640 11	6358 11	1243	0·657	0·2001650 99	6971 68	1209
0·608	0·1674998 22	6370 54	1243	0·658	0·2008622 67	6983 76	1208
0·609	0·1681368 76	6382 97	1243	0·659	0·2015606 43	6995 83	1207
0·610	0·1687751 73			0·660	0·2022602 26		
		6395 39	1242			7007 89	1206
0·611	0·1694147 12	6407 81	1242	0·661	0·2029610 15	7019 94	1205
0·612	0·1700554 93	6420 21	1240	0·662	0·2036630 09	7031 99	1205
0·613	0·1706975 14	6432 62	1241	0·663	0·2043662 08	7044 03	1204
0·614	0·1713407 76	6445 02	1240	0·664	0·2050706 11	7056 05	1202
0·615	0·1719852 78	6457 40	1238	0·665	0·2057762 16	7068 07	1202
0·616	0·1726310 18	6469 79	1239	0·666	0·2064830 23	7080 09	1202
0·617	0·1732779 97	6482 17	1238	0·667	0·2071910 32	7092 09	1200
0·618	0·1739262 14	6494 54	1237	0·668	0·2079002 41	7104 08	1199
0·619	0·1745756 68	6506 91	1237	0·669	0·2086106 49	7116 06	1198
0·620	0·1752263 59			0·670	0·2093222 55		
		6519 27	1236			7128 03	1197
0·621	0·1758782 86	6531 63	1236	0·671	0·2100350 58	7140 00	1197
0·622	0·1765314 49	6543 97	1234	0·672	0·2107490 58	7151 96	1196
0·623	0·1771858 46	6556 31	1234	0·673	0·2114642 54	7163 90	1194
0·624	0·1778414 77	6568 65	1234	0·674	0·2121806 44	7175 84	1194
0·625	0·1784983 42	6580 97	1232	0·675	0·2128982 28	7187 76	1192
0·626	0·1791564 39	6593 30	1233	0·676	0·2136170 04	7199 68	1192
0·627	0·1798157 69	6605 61	1231	0·677	0·2143369 72	7211 59	1191
0·628	0·1804763 30	6617 92	1231	0·678	0·2150581 31	7223 49	1190
0·629	0·1811381 22	6630 22	1230	0·679	0·2157804 80	7235 38	1189
0·630	0·1818011 44			0·680	0·2165040 18		
		6642 51	1229			7247 26	1188
0·631	0·1824653 95	6654 80	1229	0·681	0·2172287 44	7259 13	1187
0·632	0·1831308 75	6667 09	1227	0·682	0·2179546 57	7270 98	1185
0·633	0·1837975 84	6679 36	1226	0·683	0·2186817 55	7282 83	1185
0·634	0·1844655 20	6691 62	1226	0·684	0·2194100 38	7294 67	1184
0·635	0·1851346 82	6703 88	1226	0·685	0·2201395 05	7306 50	1183
0·636	0·1858050 70	6716 14	1224	0·686	0·2208701 55	7318 32	1182
0·637	0·1864766 84	6728 38	1224	0·687	0·2216019 87	7330 13	1181
0·638	0·1871495 22	6740 62	1224	0·688	0·2223350 00	7341 92	1179
0·639	0·1878235 84	6752 85	1223	0·689	0·2230691 92	7353 71	1179
0·640	0·1884988 69			0·690	0·2238045 63		
		6765 07	1222			7365 49	1178
0·641	0·1891753 76	6777 29	1222	0·691	0·2245411 12	7377 26	1177
0·642	0·1898531 05	6789 49	1220	0·692	0·2252788 38	7389 01	1175
0·643	0·1905320 54	6801 70	1221	0·693	0·2260177 39	7400 76	1175
0·644	0·1912122 24	6813 89	1219	0·694	0·2267578 15	7412 49	1173
0·645	0·1918936 13	6826 08	1219	0·695	0·2274990 64	7424 22	1173
0·646	0·1925762 21	6938 25	1217	0·696	0·2282414 86	7435 93	1171
0·647	0·1932600 46	6850 42	1217	0·697	0·2289850 79	7447 63	1170
0·648	0·1939450 88	6862 58	1216	0·698	0·2297298 42	7459 32	1169
0·649	0·1946313 46	6874 74	1216	0·699	0·2304757 74	7471 01	1169

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·700	0·2312228 75			0·750	0·2700408 35		
		7482 68	1167			8050 50	1103
0·701	0·2319711 43	7494 33	1165	0·751	0·2708458 85	8061 51	1101
0·702	0·2327205 76	7505 98	1165	0·752	0·2716520 36	8072 51	1100
0·703	0·2334711 74	7517 62	1164	0·753	0·2724592 87	8083 49	1098
0·704	0·2342229 36	7529 24	1162	0·754	0·2732676 36	8094 46	1097
0·705	0·2349758 60	7540 85	1161	0·755	0·2740770 82	8105 41	1095
0·706	0·2357299 45	7552 45	1160	0·756	0·2748876 23	8116 35	1094
0·707	0·2364851 90	7564 05	1160	0·757	0·2756992 58	8127 26	1091
0·708	0·2372415 95	7575 63	1158	0·758	0·2765119 84	8138 17	1091
0·709	0·2379991 58	7587 19	1156	0·759	0·2773258 01	8149 07	1090
0·710	0·2387578 77			0·760	0·2781407 08		
		7598 74	1155			8159 95	1088
0·711	0·2395177 51	7610 29	1155	0·761	0·2789567 03	8170 80	1085
0·712	0·2402787 80	7621 82	1153	0·762	0·2797737 83	8181 64	1084
0·713	0·2410409 62	7633 34	1152	0·763	0·2805919 47	8192 48	1084
0·714	0·2418042 96	7644 84	1150	0·764	0·2814111 95	8203 29	1081
0·715	0·2425687 80	7656 34	1150	0·765	0·2822315 24	8214 08	1079
0·716	0·2433344 14	7667 83	1149	0·766	0·2830529 32	8224 87	1079
0·717	0·2441011 97	7679 30	1147	0·767	0·2838754 19	8235 63	1076
0·718	0·2448691 27	7690 75	1145	0·768	0·2846989 82	8246 38	1075
0·719	0·2456382 02	7702 20	1145	0·769	0·2855236 20	8257 11	1073
0·720	0·2464084 22			0·770	0·2863493 31		
		7713 63	1143			8267 83	1072
0·721	0·2471797 85	7725 06	1143	0·771	0·2871761 14	8278 53	1070
0·722	0·2479522 91	7736 46	1140	0·772	0·2880039 67	8289 21	1068
0·723	0·2487259 37	7747 86	1140	0·773	0·2888328 88	8299 88	1067
0·724	0·2495007 23	7759 24	1138	0·774	0·2896628 76	8310 53	1065
0·725	0·2502766 47	7770 61	1137	0·775	0·2904939 29	8321 16	1063
0·726	0·2510537 08	7781 97	1136	0·776	0·2913260 45	8331 78	1062
0·727	0·2518319 05	7793 32	1135	0·777	0·2921592 23	8342 38	1060
0·728	0·2526112 37	7804 65	1133	0·778	0·2929934 61	8352 96	1058
0·729	0·2533917 02	7815 96	1131	0·779	0·2938287 57	8363 53	1057
0·730	0·2541732 98			0·780	0·2946651 10		
		7827 27	1131			8374 08	1055
0·731	0·2549560 25	7838 56	1129	0·781	0·2955025 18	8384 61	1053
0·732	0·2557398 81	7849 84	1128	0·782	0·2963409 79	8395 12	1051
0·733	0·2565248 65	7861 10	1126	0·783	0·2971804 91	8405 62	1050
0·734	0·2573109 75	7872 36	1126	0·784	0·2980210 53	8416 10	1048
0·735	0·2580982 11	7883 60	1124	0·785	0·2988626 63	8426 56	1046
0·736	0·2588865 71	7894 82	1122	0·786	0·2997053 19	8437 01	1045
0·737	0·2596760 53	7906 03	1121	0·787	0·3005490 20	8447 43	1042
0·738	0·2604666 56	7917 23	1120	0·788	0·3013937 63	8357 83	1040
0·739	0·2612583 79	7928 42	1119	0·789	0·3022395 46	8468 23	1040
0·740	0·2620512 21			0·790	0·3030863 69		
		7939 58	1116			8478 60	1037
0·741	0·2628451 79	7950 74	1116	0·791	0·3039342 29	8488 96	1036
0·742	0·2636402 53	7961 88	1114	0·792	0·3047831 25	8499 29	1033
0·743	0·2644364 41	7973 01	1113	0·793	0·3056330 54	8509 60	1031
0·744	0·2652337 42	7984 12	1111	0·794	0·3064840 14	8519 91	1031
0·745	0·2660321 54	7995 22	1110	0·795	0·3073360 05	8530 19	1028
0·746	0·2668316 76	8006 31	1109	0·796	0·3081890 24	8540 44	1025
0·747	0·2676323 07	8017 38	1107	0·797	0·3090430 68	8550 69	1025
0·748	0·2684340 45	8028 43	1105	0·798	0·3098981 37	8560 92	1023
0·749	0·2692368 88	8039 47	1104	0·799	0·3107542 29	8571 12	1020

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·800	0·3116113 41			0·850	0·3557231 13		
		8581 30	1018			9063 94	909
0·801	0·3124694 71			0·851	0·3566295 07		
		8591 47	1017			9073 01	907
0·802	0·3133286 18			0·852	0·3575368 08		
		8601 62	1015			9082 05	904
0·803	0·3141887 80			0·853	0·3584450 13		
		8611 75	1013			9091 06	901
0·804	0·3150499 55			0·854	0·3593541 19		
		8621 85	1010			9100 06	900
0·805	0·3159121 40			0·855	0·3602641 25		
		8631 95	1010			9109 03	897
0·806	0·3167753 35			0·856	0·3611750 28		
		8642 02	1007			9117 96	893
0·807	0·3176395 37			0·857	0·3620868 24		
		8652 06	1004			9126 88	892
0·808	0·3185047 43			0·858	0·3629995 12		
		8662 09	1003			9135 77	889
0·809	0·3193709 52			0·859	0·3639130 89		
		8672 10	1001			9144 63	886
0·810	0·3202381 62			0·860	0·3648275 52		
		8682 10	1000			9153 47	884
0·811	0·3211063 72			0·861	0·3657428 99		
		8692 07	997			9162 28	881
0·812	0·3219755 79			0·862	0·3666591 27		
		8702 01	994			9171 06	878
0·813	0·3228457 80			0·863	0·3675762 33		
		8711 94	993			9179 82	876
0·814	0·3237169 74			0·864	0·3684942 15		
		8721 85	991			9188 54	872
0·815	0·3245891 59			0·865	0·3694130 69		
		8731 74	989			9197 25	871
0·816	0·3254623 33			0·866	0·3703327 94		
		8741 61	987			9205 92	867
0·817	0·3263364 94			0·867	0·3712533 86		
		8751 45	984			9214 56	864
0·818	0·3272116 39			0·868	0·3721748 42		
		8761 28	983			9223 19	863
0·819	0·3280877 67			0·869	0·3730971 61		
		8771 08	980			9231 78	859
0·820	0·3289648 75			0·870	0·3740203 39		
		8780 86	978			9240 35	857
0·821	0·3298429 61			0·871	0·3749443 74		
		8790 63	977			9248 88	853
0·822	0·3307220 24			0·872	0·3758692 62		
		8800 37	974			9257 38	850
0·823	0·3316020 61			0·873	0·3767950 00		
		8810 09	972			9265 86	848
0·824	0·3324830 70			0·874	0·3777215 86		
		8819 78	969			9274 32	846
0·825	0·3333650 48			0·875	0·3786490 18		
		8829 46	968			9282 74	842
0·826	0·3342479 94			0·876	0·3795772 92		
		8839 11	965			9291 13	839
0·827	0·3351319 05			0·877	0·3805064 05		
		8848 75	964			9299 49	836
0·828	0·3360167 80			0·878	0·3814363 54		
		8858 36	961			9307 83	834
0·829	0·3369026 16			0·879	0·3823671 37		
		8867 94	958			9316 14	831
0·830	0·3377894 10			0·880	0·3832987 51		
		8877 51	957			9324 41	827
0·831	0·3386771 61			0·881	0·3842311 92		
		8887 05	954			9332 65	824
0·832	0·3395658 66			0·882	0·3851644 57		
		8896 57	952			9340 87	822
0·833	0·3404555 23			0·883	0·3860985 44		
		8906 07	950			9349 05	818
0·834	0·3413461 30			0·884	0·3870334 49		
		8915 55	948			9357 21	816
0·835	0·3422376 85			0·885	0·3879691 70		
		8925 00	945			9365 33	812
0·836	0·3431301 85			0·886	0·3889057 03		
		8934 42	942			9373 42	809
0·837	0·3440236 27			0·887	0·3898430 45		
		8943 83	941			9381 49	807
0·838	0·3449180 10			0·888	0·3907811 94		
		8953 21	938			9389 52	803
0·839	0·3458133 31			0·889	0·3917201 46		
		8962 58	937			9397 52	800
0·840	0·3467095 89			0·890	0·3926598 98		
		8971 91	933			9405 48	796
0·841	0·3476067 80			0·891	0·3936004 46		
		8981 22	931			9413 42	794
0·842	0·3485049 02			0·892	0·3945417 88		
		8990 51	929			9421 32	790
0·843	0·3494039 53			0·893	0·3954839 20		
		8999 77	926			9429 20	788
0·844	0·3503039 30			0·894	0·3964268 40		
		9009 01	924			9437 04	784
0·845	0·3512048 31			0·895	0·3973705 44		
		9018 23	922			9444 84	780
0·846	0·3521066 54			0·896	0·3983150 28		
		9027 42	919			9452 61	777
0·847	0·3530093 96			0·897	0·3992602 89		
		9036 59	917			9460 36	775
0·848	0·3539130 55			0·898	0·4002063 25		
		9045 73	914			9468 06	770
0·849	0·3548176 28			0·899	0·4011531 31		
		9054 85	912			9475 73	767

TABLE I (*continued*).

m.	*p.*	Differences. 1st.	2nd.	*m.*	*p.*	Differences. 1st.	2nd.
0·900	0·4021007 04		764	0·950	0·4503755 11		554
		9483 37				9815 83	
0·901	0·4030490 41		761	0·951	0·4513570 94		550
		9490 98				9821 33	
0·902	0·4039981 39		757	0·952	0·4523392 27		545
		9498 55				9826 78	
0·903	0·4049479 94		754	0·953	0·4533219 05		539
		9506 09				9832 17	
0·904	0·4058986 03		750	0·954	0·4543051 22		533
		9513 59				9837 50	
0·905	0·4068499 62		746	0·955	0·4552888 72		528
		9521 05				9842 78	
0·906	0·4078020 67		744	0·956	0·4562731 50		522
		9528 49				9848 00	
0·907	0·4087549 16		739	0·957	0·4572579 50		517
		9535 88				9853 17	
0·908	0·4097085 04		736	0·958	0·4582432 67		511
		9543 24				9858 28	
0·909	0·4106628 28		733	0·959	0·4592290 95		504
		9550 57				9863 32	
0·910	0·4116178 85		728	0·960	0·4602154 27		499
		9557 85				9868 31	
0·911	0·4125736 70		726	0·961	0·4612022 58		493
		9565 11				9873 24	
0·912	0·4135301 81		721	0·962	0·4621895 82		488
		9572 32				9878 12	
0·913	0·4144874 13		717	0·963	0·4631773 94		480
		9579 49				9882 92	
0·914	0·4154453 62		714	0·964	0·4641656 86		474
		9586 63				9887 66	
0·915	0·4164040 25		711	0·965	0·4651544 52		468
		9593 74				9892 34	
0·916	0·4173633 99		706	0·966	0·4661436 86		462
		9600 80				9896 96	
0·917	0·4183234 79		703	0·967	0·4671333 82		455
		9607 83				9901 51	
0·918	0·4192842 62		698	0·968	0·4681235 33		448
		9614 81				9905 99	
0·919	0·4202457 43		695	0·969	0·4691141 32		441
		9621 76				9910 40	
0·920	0·4212079 19		691	0·970	0·4701051 72		434
		9628 67				9914 74	
0·921	0·4221707 86		687	0·971	0·4710966 46		428
		9635 54				9919 02	
0·922	0·4231343 40		682	0·972	0·4720885 48		420
		9642 36				9923 22	
0·923	0·4240985 76		679	0·973	0·4730808 70		413
		9649 15				9927 35	
0·924	0·4250634 91		676	0·974	0·4740736 05		405
		9655 91				9931 40	
0·925	0·4260290 82		670	0·975	0·4750667 45		398
		9662 61				9935 38	
0·926	0·4269953 43		666	0·976	0·4760602 83		389
		9669 27				9939 27	
0·927	0·4279622 70		663	0·977	0·4770542 10		382
		9675 90				9943 09	
0·928	0·4289298 60		658	0·978	0·4780485 19		373
		9682 48				9946 82	
0·929	0·4298981 08		655	0·979	0·4790432 01		366
		9689 03				9950 48	
0·930	0·4308670 11		649	0·980	0·4800382 49		356
		9695 52				9954 04	
0·931	0·4318365 63		645	0·981	0·4810336 53		347
		9701 97				9957 51	
0·932	0·4328067 60		641	0·982	0·4820294 04		339
		9708 38				9960 90	
0·933	0·4337775 98		637	0·983	0·4830254 94		330
		9714 75				9964 20	
0·934	0·4347490 73		633	0·984	0·4840219 14		319
		9721 08				9967 39	
0·935	0·4357211 81		627	0·985	0·4850186 53		309
		9727 35				9970 48	
0·936	0·4366939 16		623	0·986	0·4860157 01		299
		9733 58				9973 47	
0·937	0·4376672 74		619	0·987	0·4870130 48		289
		9739 77				9976 36	
0·938	0·4386412 51		614	0·988	0·4880106 84		277
		9745 91				9979 13	
0·939	0·4396158 42		610	0·989	0·4890085 97		266
		9752 01				9981 79	
0·940	0·4405910 43		604	0·990	0·4900067 76		253
		9758 05				9984 32	
0·941	0·4415668 48		600	0·991	0·4910052 08		241
		9764 05				9986 73	
0·942	0·4425432 53		596	0·992	0·4920038 81		226
		9770 01				9988 99	
0·943	0·4435202 54		590	0·993	0·4930027 80		212
		9775 91				9991 11	
0·944	0·4444978 45		585	0·994	0·4940018 91		197
		9781 76				9993 08	
0·945	0·4454760 21		581	0·995	0·4950011 99		180
		9787 57				9994 88	
0·946	0·4464547 78		576	0·996	0·4960006 87		160
		9793 33				9996 48	
0·947	0·4474341 11		570	0·997	0·4970003 35		139
		9799 03				9997 87	
0·948	0·4484140 14		565	0·998	0·4980001 22		113
		9804 68				9999 00	
0·949	0·4493944 82		561	0·999	0·4990000 22		78
		9810 29				9999 78	
				1·000	0·5000000 00		22

Tables I and II.

Corrections, expressed as fractions of total capacity of tank, to be applied to calibration as obtained for a horizontal tank.

Corrections to be *added* for *lower* half of tank, and *subtracted* for *upper* half of tank.

Table II. $s = 0{\cdot}05$.

$\frac{h}{d}$.		Correction.	Differences. 1st.	2nd.
0·51	0·49	0·0000053	53	—
0·52	0·48	0·0000106	53	—
0·53	0·47	0·0000159	54	—
0·54	0·46	0·0000213	54	—
0·55	0·45	0·0000267	54	—
0·56	0·44	0·0000321	55	—
0·57	0·43	0·0000376	55	—
0·58	0·42	0·0000431	55	—
0·59	0·41	0·0000486	56	—
0·60	0·40	0·0000542	57	—
0·61	0·39	0·0000599	57	—
0·62	0·38	0·0000656	58	—
0·63	0·37	0·0000714	60	—
0·64	0·36	0·0000774	61	—
0·65	0·35	0·0000835	62	—
0·66	0·34	0·0000897	63	—
0·67	0·33	0·0000960	64	—
0·68	0·32	0·0001024	66	—
0·69	0·31	0·0001090	68	—
0·70	0·30	0·0001158	70	—
0·71	0·29	0·0001228	73	—
0·72	0·28	0·0001301	75	—
0·73	0·27	0·0001376	77	—
0·74	0·26	0·0001453	80	—
0·75	0·25	0·0001533	83	—
0·76	0·24	0·0001616	87	4
0·77	0·23	0·0001703	91	4
0·78	0·22	0·0001794	96	5
0·79	0·21	0·0001890	101	5
0·80	0·20	0·0001991	107	6
0·81	0·19	0·0002098	114	7
0·82	0·18	0·0002212	121	7
0·83	0·17	0·0002333	130	9
0·84	0·16	0·0002463	141	11
0·85	0·15	0·0002604	153	12
0·86	0·14	0·0002757	167	14
0·87	0·13	0·0002924	185	18
0·88	0·12	0·0003109	206	21
0·89	0·11	0·0003315	232	26
0·90	0·10	0·0003547	266	34
0·91	0·09	0·0003813	311	45
0·92	0·08	0·0004124	372	61
0·93	0·07	0·0004496	455	83
0·94	0·06	0·0004951	586	131
0·95	0·05	0·0005537		

Table III. $s = 0{\cdot}01$.

$\frac{h}{d}$.		Correction.	Differences. 1st.	2nd.
0·51	0·49	0·0000002	2	—
0·52	0·48	0·0000004	3	—
0·53	0·47	0·0000007	2	—
0·54	0·46	0·0000009	2	—
0·55	0·45	0·0000011	2	—
0·56	0·44	0·0000013	2	—
0·57	0·43	0·0000015	2	—
0·58	0·42	0·0000017	2	—
0·59	0·41	0·0000019	3	—
0·60	0·40	0·0000022	2	—
0·61	0·39	0·0000024	2	—
0·62	0·38	0·0000026	3	—
0·63	0·37	0·0000029	2	—
0·64	0·36	0·0000031	2	—
0·65	0·35	0·0000033	3	—
0·66	0·34	0·0000036	2	—
0·67	0·33	0·0000038	3	—
0·68	0·32	0·0000041	3	—
0·69	0·31	0·0000044	2	—
0·70	0·30	0·0000046	3	—
0·71	0·29	0·0000049	3	—
0·72	0·28	0·0000052	3	—
0·73	0·27	0·0000055	3	—
0·74	0·26	0·0000058	3	—
0·75	0·25	0·0000061	4	—
0·76	0·24	0·0000065	3	—
0·77	0·23	0·0000068	4	—
0·78	0·22	0·0000072	4	—
0·79	0·21	0·0000076	4	—
0·80	0·20	0·0000080	4	—
0·81	0·19	0·0000084	5	—
0·82	0·18	0·0000089	5	—
0·83	0·17	0·0000094	5	—
0·84	0·16	0·0000099	6	—
0·85	0·15	0·0000105	6	—
0·86	0·14	0·0000111	7	—
0·87	0·13	0·0000118	7	—
0·88	0·12	0·0000125	8	—
0·89	0·11	0·0000133	9	—
0·90	0·10	0·0000142	10	—
0·91	0·09	0·0000152	12	—
0·92	0·08	0·0000164	15	—
0·93	0·07	0·0000179	18	—
0·94	0·06	0·0000197	22	4
0·95	0·05	0·0000219	30	8
0·96	0·04	0·0000249	44	14
0·97	0·03	0·0000293	71	27
0·98	0·02	0·0000364	164	93
0·99	0·01	0·0000528		

tank F. The true or vertical dip reading at this point is KF, and $h_1 = \frac{KF}{\cos\theta}$; hence $m_1 = \frac{KF}{D\cos\theta}$.

Example: Tank, 9 ft diameter, 30 ft long, with a rise of 7 inches in the length of the tank. Point at which dip readings are taken is 2·30 inches above lower corner of tank.

$$CF^2 = EF^2 - EC^2 = 129551$$
$$CF = 359{\cdot}9319$$

Calibration Constants.

$$\left.\begin{aligned}\cos\theta &= 359{\cdot}9319 \div 360\\ &= 0{\cdot}9998109\end{aligned}\right\} \ldots \text{hence,} \quad \frac{1}{D\cos\theta} = 0{\cdot}009261010$$

$$\left.\begin{aligned}\frac{L}{D}\tan\theta &= \frac{L\sin\theta}{D\cos\theta}\\ &= DH \times \frac{1}{D\cos\theta}\\ &= 7 \times 0{\cdot}009261010\end{aligned}\right\} \ldots \text{hence,} \quad s = 0{\cdot}0648271$$

$$C = 11886{\cdot}24 \text{ gallons}; \quad \ldots \text{hence,} \quad \frac{C}{s} = 1833530$$

(*Note*: Instead of working out $D\cos\theta$ and using it as a divisor for each of the dip readings, it is much simpler to obtain the reciprocal of $D\cos\theta$ and use it as a multiplier.)

The second stage of the work, namely the calculation of the quantities corresponding to the individual dip readings, is shown set out in tabular form below. It will be seen that the procedure is almost identical to that adopted for a horizontal tank except that, whereas in the latter case it is only necessary to obtain one value of the capacity coefficient for each dip reading from the appropriate table, in the present case it is necessary to obtain two values and take the difference.

TABLE IV.

Dip reading.		$m_1 = \frac{\text{Corr. dip}}{D\cos\theta}$.	$m_2 = m_1 - s$.	p_1 p_2	$p_1 - p_2$.	Gallons = $\frac{C}{s}(p_1 - p_2)$.
Actual.	Corr.					
—	—	—		—		
98	100·3	0·9290623		0·429958490		
			0·8642352	0·368710406	0·061248084	11230·02
99	101·3	0·9383251		0·438958158		
			0·8734980	0·377256546	0·061701612	11313·18
100	102·3	0·9475879		0·448010264		
			0·8827608	0·385875184	0·062135081	11392·65
101	103·3	0·9568508		0·457111051		
			0·8920237	0·394564126	0·062546925	11468·17
—	—	—	—	—	—	—

The figures have been chosen to illustrate the use of the full table and not as typical for a 30 ft × 9 ft tank. For this size of tank it would suffice to take columns 3 and 4 to the fifth and columns 5 and 6 to the seventh decimal place with the final result to the nearest gallon.

The foregoing constitutes, in effect, the whole procedure, but there are several points of detail which call for further explanation. Also, there is an alternative and simpler method of calculation which is applicable to tanks lying at a small angle of slope. These will now be dealt with.

Top and Bottom Section.

Where the liquid does not cover the bottom of the tank as at NP, Fig. 4, m_1 will be less than s and there will be no value for m_2. The general formula still holds good, but p_2 will be zero.

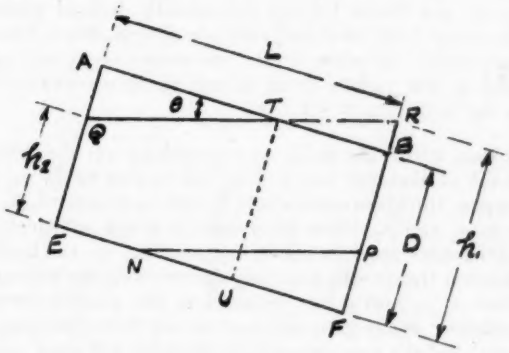

Fig. 4.

Where the level of the liquid is above the top of the lower end of the tank as at QT, Fig. 4, m_1 will be greater than unity.

Consider the cylinder $ATUE$.

Volume $= C \times \dfrac{AT}{AB}$; slope ratio $= \dfrac{AT}{D} \tan \theta$.

Hence, $\dfrac{\text{capacity}}{\text{slope ratio}} = \left(C \times \dfrac{AT}{AB}\right) \div \left(\dfrac{AT}{D} \tan \theta\right) = \dfrac{C}{s}$;

Hence by equation (4) volume of $QTUE = \dfrac{C}{s}(0{\cdot}5 - p_2)$.

Volume of cylinder $BFTU = C \times \dfrac{h_1 - D}{h_1 - h_2} = \dfrac{C}{s}(m_1 - 1)$.

Total volume of $QTBFE = \dfrac{C}{s}(m_1 - 0{\cdot}5 - p_2)$

i.e., when $m_1 > 1$, $p_1 = m_1 - 0{\cdot}5$.

It will be seen therefore that the general formula covers the full range of the tank, in all cases from 0 up to 90 degrees angle of slope.

Considerations of Accuracy.

It will be noted that in Table IV the final results are given to seven figures. It is not suggested that this degree of accuracy is necessary in a tank 9 ft diameter by 30 ft long, but it has been adopted in the present case to illustrate the degree of accuracy available.

Assuming, however, for example, that it is desired to work to seven figures in the final result, then the degree of accuracy required in the various factors entering into the calculations is as follows :—

C—to seven figures;

m_1, m_2, and s—to the seventh decimal place;

$\frac{1}{D \cos \theta}$—to seven figures beyond any 0's which appear after the decimal point;

p_1 and p_2—to one figure beyond the seventh decimal place if s is of the order 1·000 to 0·100, and two figures, if s is between 0·100 and 0·010. In other words, the values of p_1 and p_2 must be such as will yield a result correct to the seventh decimal place in the factor $(p_1 - p_2) \div s$.

If s is less than 0·010, the necessity for working out the calibration for an inclined tank is doubtful, but if it is still desired to do so, it is much simpler to employ the alternative method, still to be described.

Reverting to p_1 and p_2, linear interpolation is not sufficiently accurate and second differences must be taken into account, on the basis of recognized interpolation theory which is fully described in the literature.

Where values of p_1 and p_2 are required to the seventh decimal place, linear interpolation would give an error in no case exceeding 2, in the last figure, and over the greater range of the table the error would be less than 0·5.

It will be observed that in tabulating the values for p, the last two figures have been split off from the others. This facilitates reading off the numbers, especially when they are only required to the seventh or eighth place. The same principle has been carried out with the first differences, but not with the second differences.

Method of Corrections.

Where the slope ratio is small, say in the vicinity of 0·010 or less, but depending, too, on the degree of accuracy required, it will be found more convenient in many cases to work out the calibration as for a horizontal tank and apply a correction based on Table II or Table III.

When using this method it is first necessary to adjust all dip readings to give the corresponding reading at the centre of the tank; that is, at GS (see Fig. 5), where S is the mid-point of the tank bottom. The dip reading GS is then divided by $D \cos \theta$, not by D, to obtain the true ratio h/D. This is the invariable rule in both methods of calculation.

The fraction of the total capacity corresponding to this value of h/D is obtained from the appropriate table for horizontal tanks and a correction

applied based on Table II or Table III. These corrections are expressed as fractions of the total capacity of the tank and have no relation to Table I, except that they are derived from it. They are positive for the lower half of the tank and negative for the upper half.

Table II is for a slope ratio of 0·05 and Table III for a slope ratio of 0·01; for intermediate or lower values of s the correction is almost exactly proportional to the square of the slope ratio. For values of s less than 0·05, Table II will give results between 0·13 and 0·87 of the tank diameter in which the error should not exceed one in the seventh decimal place. Beyond these points the error increases and reaches a maximum at the lower end of the table of about eight in the last decimal place. This occurs when s is in the region of 0·02, but for this slope ratio, Table III would give more accurate results.

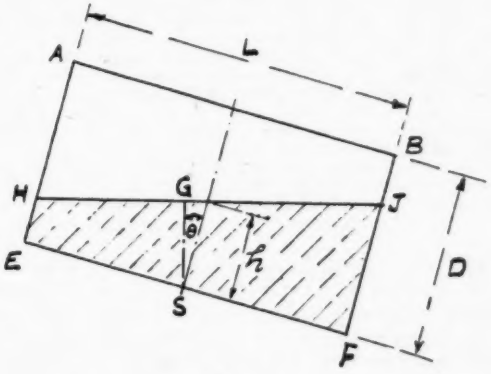

FIG. 5.

Table III is for a slope ratio of 0·01 and when used for smaller values of s, will give results in which the error does not exceed one in the seventh decimal place, over the whole range of the tabulation.

It should be noted, however, that these corrections are not applicable over a range of $\frac{1}{2}s$ from the top or bottom of the tank, but in any case, their usefulness begins to fall off rapidly at twice this range, hence the reason that the tabulations have not been taken further. For values beyond the range of the tabulations, it is necessary to use the basic method.

DISHED END TANKS.

The gallonages in the dished ends are calculated by any convenient method already available for the dished ends of horizontal tanks and added to that for the main body of the tank, but the calculation has to be done separately for each end. The gallonage at the low end is that corresponding to a height (or depth) ratio m_1 and at the high end, that corresponding to the ratio m_2.

This is not strictly accurate, as it assumes that the surface of the liquid

in the dished end is parallel to the axis of the tank, whereas it is actually inclined to the axis of the tank at an angle θ. The error is negative at the low end and positive at the high end of the tank so that the two tend to cancel out. The correction necessary at each end can be evaluated to a first degree of approximation by a comparatively simple method, but it is found that for all sizes of tanks and angles of slope normally encountered, the resultant error is negligible.

THE PRODUCTION OF OLEFIN-POLYMER LUBRICATING OILS OF SATISFACTORY OXIDATION STABILITY.

By G. H. Dazeley,* D. Gall,* and C. C. Hall.*

Summary.

Attempts have been made to increase the oxidation stability (as measured by the B.A.M. Oxidation Number test) of olefin-polymer lubricating oils derived from the products of the Fischer–Tropsch synthesis.

A controlled hydrogenation of the oils in the presence of a molybdenum disulphide catalyst at 200° C and 200 atm pressure yields an oil with an oxidation number of 1·8. The effect is the result of saturation by hydrogen coupled with the formation of sulphur-containing inhibitors and can be accurately reproduced by hydrogenation in the presence of nickel catalysts followed by heating with molybdenum disulphide in the absence of hydrogen.

Treatment of the oil with aluminium chloride at 180° C produces some improvement in oxidation stability, but the effect is small and is accompanied by a serious loss of oil.

Naphthalene added to the olefins before polymerization is chemically incorporated in the resulting oil and leads to an increase in oxidation stability, an increased conversion of the olefins to lubricating oil, but a decrease in the viscosity index of the oil. About 15 per cent of naphthalene is required to produce an oil with an oxidation number below 2·0; this causes a fall in viscosity index from 100 to a value in the range 80 to 85.

A considerable amount of work has been carried out at the Fuel Research Station during the past ten years on the preparation of lubricating oils by the polymerization, in the presence of aluminium chloride, of olefins present in the primary products of the Fischer–Tropsch synthesis,[1, 2] or derived therefrom by thermal cracking.[3, 4] The principal aim of this work was to produce an oil which would satisfy the Air Ministry specification for aircraft lubricating oils. With one exception, all the oils produced failed to satisfy this specification in respect of stability to oxidation, in that the ratio of the viscosity of the oil after oxidation under the conditions required by the specification to the original viscosity (*i.e.*, the " B.A.M. Oxidation Number " [5]) was above 2·0. The exception was an oil obtained by polymerizing the olefins distilling in the range 170° to 240° C prepared by thermal cracking of the diesel-oil fraction of the Fischer–Tropsch product.[3] This oil, which met the specification with ease, was obtainable only in low yield and as the reasons for its anomalous oxidation stability have not been established, there is an element of uncertainty as to its reproducibility. A number of attempts have therefore been made to increase the oxidation stability of olefin-polymer oils either by after-treatment of oils prepared in the usual manner or by adopting special conditions in the preparation.

An account of this work is presented in this paper.

Hydrogenation and the Introduction of Sulphur Inhibitors.

In the account of the preparation of lubricating oils by the polymerization of the olefins present in the primary products of the Fischer–Tropsch syn-

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thesis, the effect of hydrogenation of the oils in the presence of molybdenum sulphide catalyst on the oxidation number was described.[1] It was shown that when a sample of oil with an oxidation number of 3·86 was hydrogenated in an autoclave at 200° C and 200 atm pressure of hydrogen in the presence of 20 per cent by weight of pelleted molybdenum disulphide, the oxidation number fell to 1·8 and then rose again to nearly 3·0 as the time of hydrogenation increased, although the degree of hydrogenation of the oil as indicated by its physical properties showed the expected steady increase (see Table I).

TABLE I.

Properties of Oils Hydrogenated in the Presence of Molybdenum Disulphide Catalyst.

Period of hydrogenation, hours.	0.	6.	12.	24.	96.
Aniline point, ° C . . .	120·9	123·0	124·8	127·7	127·7
Refractive index, n_D^{20} . .	1·4725	1·4687	1·4678	1·4656	1·4644
B.A.M. Oxidation No. . .	3·9	1·8	2·0	2·7	2·9
Sulphur content, per cent .	0·05	0·16	0·11	0·03	—

The work of Denison [6] on the role of sulphur compounds as oxidation inhibitors in lubricating oils derived from petroleum suggested the determination of the sulphur content of the hydrogenated oils. The results are shown in Table I, from which it will be seen that the sulphur content was at a maximum for the oil with minimum oxidation number. It appeared from this that after a certain period of hydrogenation in the presence of molybdenum sulphide, sulphur compounds which functioned as oxidation inhibitors were formed, but were partially destroyed on more prolonged hydrogenation.

It therefore seemed possible that simple heating of the oils with molybdenum sulphide (or even with free sulphur) in the absence of hydrogen might confer the desired oxidation stability. Accordingly, samples of oil derived from the same stock as that employed in the earlier hydrogenation experiments were heated in evacuated sealed glass tubes for 6 hours at 200° C, (*a*) alone, (*b*) in the presence of 20 per cent of molybdenum disulphide, and (*c*) with 20 per cent of flowers of sulphur. The treated oils were diluted with petroleum ether, the mixtures filtered, washed with sodium hydroxide and water, dried, and the ether removed by distillation. The properties of the recovered oils together with those of the original stock are given in Table II.

TABLE II.

Properties of Oils after Heating with Molybdenum Disulphide or Free Sulphur.

Oil sample.	No. 1.				No. 2.	
Treatment of oil.	None.	Heated alone.	Heated with S.	Heated with MoS_2.	None.	Heated with MoS_2.
Viscosity at 100° F, cs .	130	132	132	138	185	182
B.A.M. Oxidation No. .	—	5·8	5·9	3·2	4·1	3·2
Sulphur content, per cent	0·04	0·04	0·06	0·44	0·04	0·50

It will be seen that heating with sulphur produced no significant change in the sulphur content or oxidation stability of the oil, but heating with molybdenum sulphide introduced a considerable amount of sulphur into the oil and produced a marked lowering of the oxidation number. Although the sulphur content was appreciably higher than the maximum value for oils hydrogenated in the presence of molybdenum sulphide, the oxidation number was considerably higher than the minimum value obtained by hydrogenation. It seemed clear, therefore, that hydrogenation (or the presence of hydrogen) was necessary in order to achieve the maximum increase in oxidation stability.

In order to determine the separate effect of hydrogenation, samples of the oil stock were hydrogenated in the presence of a pelleted catalyst of composition : nickel : thoria : kieselguhr = 100 : 22 : 100, reduced in hydrogen before use at 450° C for 3 hours. The conditions used and the properties of the oil before and after hydrogenation are shown in Table III.

TABLE III.

Properties of Oils Hydrogenated in the Presence of Nickel–Thoria–Kieselguhr Catalyst.

Conditions of hydrogenation :				
Temperature, ° C . .	—	135	150	195
Pressure, p.s.i. . . .	—	135	145	160
Time, hrs.	—	150	100	83
Sample.	Untreated.	A.	B.	C.
Aniline point, ° C . . .	120·9	124·2	124·8	126·6
Refractive index, n_D^{20} . .	1·4725	1·4684	1·4684	1·4672
B.A.M. Oxidation No. . .	3·9	3·4	3·5	4·0

It will be observed that the general trend of the results is similar to that obtained when using molybdenum-sulphide catalyst, in that the degree of hydrogenation of the oils (as indicated by refractive index and aniline point) increased with increase in the severity of the hydrogenation conditions while the oxidation number at first fell and then rose again. The minimum oxidation number was obtained at approximately the same degree of hydrogenation, but the actual value (3·4) was very much higher than that previously obtained (1·8).

The two oils (*A* and *B*) hydrogenated in the presence of nickel catalyst were then heated with molybdenum disulphide in sealed glass tubes in the absence of hydrogen under the same conditions as were employed above for the unhydrogenated oils. The properties of the treated oils, which are shown in Table IV, were almost identical with those of the oil of minimum

TABLE IV.

Properties of Hydrogenated Oils after Heating with Molybdenum Disulphide.

Oil sample.	A, before treatment.	A, after treatment.	B, before treatment.	B, after treatment.
B.A.M. Oxidation No. . .	3·4	1·8	3·5	1·8
Sulphur content, per cent .	0·03	0·23	0·02	0·13

oxidation number and maximum sulphur content previously obtained by hydrogenation for 6 hours in the presence of molybdenum disulphide. It will be observed that the hydrogenated oils took up only half the amount of sulphur taken up by the unhydrogenated oils, suggesting that sulphur is introduced into the oil by reaction with olefins.

It is clearly established, therefore, that the successful reduction of the oxidation number of these oils by a controlled amount of hydrogenation in the presence of molybdenum disulphide is the result of two distinct processes, saturation of olefinic linkages and the formation of organic sulphur compounds which function as oxidation inhibitors.

It is now known that olefin-polymer oils of the type studied in the present work were manufactured on an industrial scale in Germany during the period 1938 to 1945. The Germans were well aware of the low oxidation stability of these oils, but claimed that this disability could be overcome by the addition of either 0·2 to 0·5 per cent of phenthiazine or 0·1 to 0·2 per cent of free sulphur to the olefins before polymerization.[7]

This claim was given a preliminary examination by polymerizing the olefins in the fraction of material distilling below 200° C obtained by the thermal cracking of the Fischer–Tropsch diesel oil (boiling range 200° to 300° C) to which, in one case, 0·3 per cent of phenthiazine was added and in the other, 0·5 per cent of flowers of sulphur. The oxidation number of the oil obtained with the addition of phenthiazine was 2·66 and that of the oil prepared in the presence of sulphur, 3·75. No "blank" polymerization was carried out on the particular sample of cracked product used in these tests, but oils obtained from similar material had oxidation numbers ranging from 3·0 to 4·0.[3] Hence, although this claim may be worthy of more thorough investigation, it appears from these two experiments that incorporation of sulphur produces no increase, and that of phenthiazine an insufficient increase, in the oxidation stability of these oils as judged by the B.A.M. oxidation-number test.

Treatment of the Oils with Aluminium Chloride.

The Ruhrchemie A.G. have claimed [8] that the "thermal stability" of olefin-polymer lubricating oils can be improved by heating with either aluminium chloride or the aluminium-chloride sludge formed in the preparation of the oils. The effect of this treatment on the B.A.M. oxidation number of such oils was considered worth investigation.

Two samples of oil, one of very low oxidation stability, prepared from primary synthesis product, and the other, of rather higher stability, prepared from the cracked diesel-oil fraction, were heated with powdered aluminium chloride under the conditions shown in Table V. The products were diluted with light petroleum ether, the clear upper layer decanted from the sludge, refined with fullers-earth–lime mixture and filtered. The solvent was then removed by distillation at atmospheric pressure and the residue topped to 200° C at 3 mm pressure. The viscosities before and after air blowing under the conditions of the B.A.M. test were then determined.

It will be seen that although the use of 5 per cent of aluminium chloride produced an appreciable increase in the stability of the less stable oil, the treated oil was still very unstable by the Air Ministry standards. The

TABLE V.

Effect of Aluminium-chloride Treatment on Olefin-polymer Oils.

Sample of oil.	Treatment.	Loss involved in treatment (wt. per cent of original oil topped to 200° C at 3 mm).	Properties of treated oils.	
			Viscosity at 100° F, cs.	B.A.M. oxidation number.
From primary product	None	—	185	4·1
" " "	1 per cent of $AlCl_3$ for 4 hr at 180° C.	10	253	3·7
" " "	5 per cent of $AlCl_3$ for 2 hr at 180° C.	37	263	3·3
From cracked diesel oil	None	—	214	2·7
" "	5 per cent of $AlCl_3$ for 2 hr at 180° C.	33	188	2·6

treatment effected no significant improvement in the oxidation stability of the more stable oil.

The severe losses incurred in the more drastic treatment, which are partly due to cracking of the oil to lower-boiling products and partly to sludge formation, would in any case make this method of refining unattractive.

THE INCORPORATION OF NAPHTHALENE IN THE POLYMERIZATION.

It is known that the presence of certain alkyl naphthalenes in lubricating oils will retard the oxidation of the oil by air or oxygen,[9] and that synthetic lubricating oils prepared by the Friedel–Craft condensation of chlorinated paraffin wax and naphthalene have been shown [10] to have oxidation numbers below 2·0. In view of the fact that olefins readily condense with aromatic hydrocarbons in the presence of aluminium chloride, it was expected that the addition of naphthalene to the reaction mixture of olefins and aluminium chloride used in the preparation of olefin-polymer lubricating oils might, therefore, lead to the chemical incorporation of the naphthalene and give oils of low oxidation number.

Polymerization experiments were carried out using as raw material the combined highly unsaturated fractions (b. p. below 200° C) obtained by thermal cracking of Fischer–Tropsch diesel oil and wax to which were added various proportions (0 to 20 per cent) of pure naphthalene. The naphthalene was dissolved in the cracked spirit by stirring at 35° C and the polymerization was then carried out in the usual manner with the addition of aluminium chloride (3 per cent by weight of the spirit). The presence of naphthalene in the reaction mixture caused a marked increase in the vigour of the reaction. With 20 per cent, the temperature rose rapidly and uncontrollably to 140° C and had to be checked by water-cooling. With 10 per cent, a similar sudden rise occurred after an initial steady rise to 75° C and with 5 per cent a less violent effect was observed after a much

longer delay. The temperature in these two cases was controlled at 100° C until the initial reaction subsided. In each case the mixture was maintained for a period of 2 hours at 80° C. After cooling, the mixture was diluted with petroleum ether (b. p. 60° to 80° C), the clear upper layer decanted, refined with fullers-earth–lime mixture, filtered, and the oil recovered as the residue above 200° C at 3 mm pressure. In the experiment with 20 per cent of naphthalene some unchanged naphthalene distilled off with the light oil, but in the other cases no unchanged naphthalene was detected.

The yields and properties of the oils obtained are given in Table VI.

TABLE VI.

Yields and Properties of Lubricating Oils Obtained by Polymerization of Olefins in the Presence of Naphthalene.

Experiment number.	Naphthalene added, wt. per cent of cracked spirit.	Yield of lubricating oil, wt. per cent of total starting material including naphthalene.	Yield of light oil, wt. per cent of total starting material.	Properties of lubricating oils.				
				Density, d_4^{20}.	Refractive index, n_D^{20}.	Viscosity at 100° F, cs.	Viscosity index.	B.A.M. oxidation number.
1	20	77	11	0·891	1·5050	391	80	1·7
2	10	71	15	0·879	1·4895	300	86	2·0
3	5	58	20	0·868	1·4812	223	96	2·5
4	0	51	22	0·858	1·4723	156	100	2·9

In the first place, these results show that the addition of naphthalene effects a more complete conversion of the olefins to material in the lubricating-oil range, since the increase in yield over that obtained in the blank experiment is in each case greater than can be accounted for even assuming 100 per cent incorporation into the lubricating oil of the naphthalene added. A correspondingly smaller proportion of the product appears in the light-oil range.

The densities and refractive indices of the oils accord with the incorporation of progressively greater amounts of naphthalene, the effect of which on viscosity, viscosity index, and oxidation number is clearly marked and regular. There is a definite increase in oxidation stability with increasing addition of naphthalene, the value of 1·7 for the oil produced in Experiment 1, with 20 per cent of naphthalene being sufficiently low to meet the Air Ministry specification. In view of the fact that in this case the naphthalene was not completely incorporated and that the addition of 10 per cent in Experiment 2 gave an oil of border-line stability, it can be concluded that addition of about 15 per cent of naphthalene is necessary to achieve a satisfactory oxidation stability. It will be observed that the viscosity of the oils increased with increase in the proportion of naphthalene added, but that the viscosity index decreased. With the proportion of naphthalene necessary to produce the required increase in oxidation

stability, the viscosity index falls by 15 to 20 per cent. Although a viscosity index of 80 to 85 is still very satisfactory, it is unfortunate that in overcoming the main weakness of these oils (their low oxidation stability) their outstandingly good viscosity–temperature properties become impaired. The introduction of aromatic nuclei into the oils would be expected to have this effect.

ACKNOWLEDGMENTS.

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THE IMPORTANCE OF CHEMICAL ATTACK IN THE LUBRICATION OF METALS.*

F. P. Bowden. †

The object of this introductory note is to emphasize one point in the theory of boundary lubrication: that is, the importance of chemical attack of the surface.

It has been customary in the past to consider that boundary lubrication by long-chain fatty acids, and by other hydrocarbons, was due to an oriented layer of molecules adsorbed at the surface.

A few simple experiments show that this is an over-simplification. Let us consider first the effect of temperature on boundary lubrication. If the friction between metal surfaces which are lubricated by hydrocarbon films is measured, it will be found that, in general, the friction does not vary continuously with temperature; there is usually a sharp rise, or transition, in the friction when a certain temperature is reached. If one of the moving

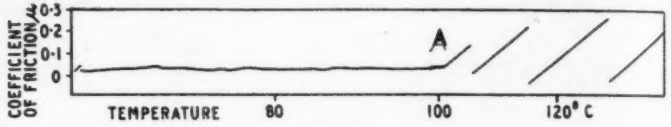

Fig. 1.

EFFECT OF TEMPERATURE ON FRICTION OF CADMIUM SURFACES LUBRICATED BY 1 PER CENT LAURIC ACID IN PARAFFIN OIL.

surfaces possesses an appreciable degree of elastic freedom, there may at this point be a change from smooth sliding to "stick-slip" motion. This is illustrated by Fig. 1, which shows the effect of temperature on the friction of cadmium surfaces lubricated by 1 per cent lauric acid in paraffin oil. The change in the friction at the point A is accompanied by a marked increase in the wear or damage of the surfaces. This is illustrated by Fig. 2.

Now at what temperature does this transition occur? In the case of saturated hydrocarbons, long-chain alcohols, etc., it is simple—it occurs at the melting point. If, for example, docosane (m. pt. 43° C) is taken, it gives a low friction and smooth sliding until a temperature of 43° C is reached, when there is a sudden rise in the friction. This is true whether it is present as a single layer or whether several layers are present. It is also true whatever the nature of the underlying metal. The same thing is found for the long-chain alcohols. For example, with cetyl alcohol (C_{16}) (m. pt. 49·3° C) the transition temperature is 49° to 50° C and again is independent of the nature of the underlying metal. With lubrication by thin

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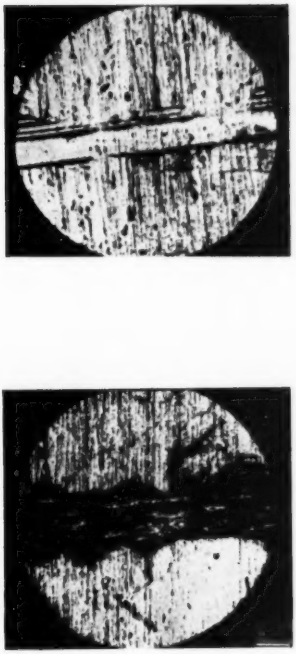

FIG. 2.

TRACK WEAR, ZINC SURFACES WITH 1 PER CENT PALMITIC ACID IN PARAFFIN—(*top*) BELOW TRANSITION TEMPERATURE, AND (*lower*) ABOVE TRANSITION TEMPERATURE. (× 25.)

[*To face p.* 654.

films of soft metals, a similar effect is observed. For example, steel or copper surfaces may be lubricated by thin films of indium or lead. Again, there is a transition temperature which corresponds to the melting point of the indium or lead. The explanation of this is obvious and it shows that the lateral adhesion between the molecules of the boundary film is of primary importance in protecting the surfaces, and in diminishing the extent to which contact can occur through the film. When the temperature is raised and melting and disorientation occurs, this lateral adhesion is diminished, breakdown of the film and increased solid contact and damage take place through the film. The effect is reversible, and on cooling, the transition to a low friction occurs at the same temperature.

It is when the fatty acids on metals are studied that the apparent anomalies occur. If, for example, the lubrication of steel surfaces by fatty acids is considered, it is found that there is a transition temperature, but it does not occur at the melting point of the fatty acid—it is very considerably higher. For example, lauric acid (m. pt. 44° C) will lubricate steel quite well until a temperature of *ca* 110° C is reached, *i.e.*, the transition temperature or the breakdown temperature is some 60° to 70° C above the melting point of the fatty acid. This behaviour is quite general. It is true for all fatty acids on steel. The breakdown temperature depends, to a certain extent, upon the load and conditions of sliding, but it is always very considerably higher than the melting point of the acid.

Why is this? The reason is fairly clear if the lubrication of a number of metals is studied, and at the same time the extent to which the fatty acid can react with the metal is taken into account. Gregory's results for a number of different metals are shown in Table I.[1] We see that the metals fall into two classes—those which are attacked by the fatty acid, and those

TABLE I.

Efficiency of Lubrication with 1 per cent Lauric Acid in Paraffin Oil compared with Reactivity of the Metal to Lauric Acid.

Metal.	Coeff. of friction (20° C).	Transition temperature, ° C.	% acid reacting (Table IV).	Type of sliding at 20° C.
Zinc	0·04	94	10·0	Smooth
Cadmium	0·05	103	9·3	„
Copper	0·10	97	4·6	„
Magnesium	0·10	80	Trace	„
Iron	0·15–0·20	*ca* 40–50	„	Irregular smooth
Platinum	0·25	< 20	0·0	Stick-slip
Nickel	0·28	< 20	0·0	„
Aluminium	0·30	< 20	0·0	„
Chromium	0·34	< 20	Trace	„
Glass	0·3–0·4	< 20	0·0	Stick-slip (irregular)
Silver	0·55	< 20	0·0	„ (large)

which are not. It is probable that attack occurs via the oxide film. The striking result from the frictional point of view is that on the unreactive metals, such as nickel, platinum, silver, and chromium, fatty acids are scarcely more effective as lubricants than saturated hydrocarbons. This

at once leads to a modification of the older theory that boundary lubrication is due to an adsorbed monolayer, and suggests that fatty acids are most effective as boundary lubricants only when they can react with the surface to form the metallic soap, *i.e.*, the lubrication is effected *not* by the adsorbed layer of fatty acid itself, but by the metallic soap formed on the metal surface.

This view has been confirmed by experiments on the lubricating properties of metal soaps. The results show that in many cases, the frictional properties of a fatty acid R—COOH on a metal surface M are the same as those obtained with the soap R—COOM on *any* surface. Further, the transition temperature at which lubrication breaks down corresponds approximately to the *softening point* of the metallic soap.

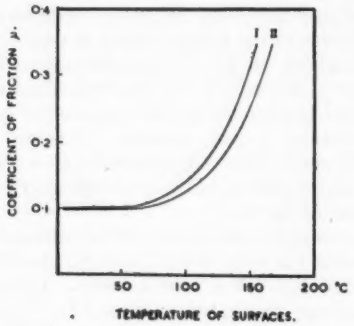

FIG. 3.

EFFECT OF TEMPERATURE ON FRICTION.
I. SOLID COPPER LAURATE (SOFTENING POINT 110° C) ON PLATINUM SURFACES.
II. 1 PER CENT LAURIC ACID IN PARAFFIN OIL ON COPPER SURFACES.

For example, when a 1 per cent solution of lauric acid is used on cadmium, it reacts to form a soap, and the behaviour is the same as when the surface is lubricated with cadmium laurate. The friction is small ($\mu = 0{\cdot}05$), and this low friction is maintained up to a temperature of *ca* 100° C, which corresponds to the softening point or melting point of the soap film. Similar results are obtained with copper surfaces and copper laurate (Fig. 3).

When the same solution of lauric acid is used on silver surfaces, it does not react, so that it is relatively ineffective as a lubricant, and even at low temperatures the friction is high ($\mu = 0{\cdot}55$ at 20° C).

The main purpose of the lubricant film is to reduce the amount of metallic contact between the surfaces by interposing a layer that is not easily penetrated and that possesses a relatively low shear strength. In order to prevent appreciable contact, the lubricating layer must, in addition to being firmly attached to the surface, possess a strong lateral adhesion between the hydrocarbon chains. If the film softens, melts, or "expands," that is, if the lateral adhesion between the chains falls to a low value, metallic seizure occurs with a corresponding increase in friction and wear. The fact that *solid* films of saturated hydrocarbons are more effective in lubricating unreactive metals than fatty acids above their melting point

shows that the strength of the lateral adhesion between the large hydrocarbon molecules is at least as important as the strength of attachment to the surface.

As shown, at the loads used in these experiments, fatty acids in themselves are scarcely more effective than saturated hydrocarbons as boundary lubricants when applied to unreactive surfaces. Even when they form well-adsorbed and oriented films on platinum or nickel surfaces, they do not lubricate above their bulk melting points. This means that even the longest-chain fatty acids do not lubricate unreactive surfaces at temperatures above about 90° C. The softening points of metallic soaps, however, are usually very much higher than the melting points of the pure acids. For this reason fatty acids are much more effective as boundary lubricants at heavy loads and high temperatures if they are used in the form of metallic soaps. This may be achieved by applying them to metal surfaces with which they react. The metal soap is then formed *in situ* and is well attached to the surface. In many cases even a monolayer of such a film is sufficient to prevent much penetration and metallic contact; in other cases, however, appreciably thicker films may be necessary. These soap films maintain their lubricating properties with increasing temperature until the softening point of the soap is reached. At this stage the film softens or melts, and increased metallic contact occurs through it, with corresponding increase in friction and wear. As the soap film loses its lateral adhesion, its linkage to the metal surface also grows weaker, and the breakdown of the lubricant film is often accompanied by its dissolution into the superincumbent oil or excess acid.

If the metal surface is unreactive, the fatty acid will not lubricate above its bulk melting point, and must be applied as a metallic soap. In such cases the physical texture and the mode of deposition of these films may be very important. The best frictional properties are obtained when the soap film has a close coherent texture, is evenly deposited over the surface, and is firmly adsorbed. These films will lubricate until the softening point of the soap occurs. If, however, the adsorption of the soap to the surface is weak and there is a superincumbent layer of oil present, it may dissolve in the excess oil at a temperature lower than its softening point. In this case, breakdown of the lubricant film will occur at temperatures below the softening point of the metallic soap.

The softening point of a soap is not clearly defined and may cover a wide temperature range. The actual temperature at which the weakening of the soap film is sufficient to cause an appreciable increase in metallic seizure (and hence in the friction and wear) will clearly depend on the physical conditions of the experiment. With hard surfaces, where the pressures are high, or with extremely slow surface speeds, the breakdown should be discernible at lower temperatures. This is generally found to be so; with any given metal and lubricant the transition temperature is dependent in this way upon the load, speed, and shape of the sliding surfaces.

The action of fatty acids in lubricating metal surfaces, therefore, bears some resemblance to that of the so-called " extreme pressure " lubricants in that chemical attack of the surfaces is important. Some accounts of the mechanism of lubrication by active compounds containing chlorine and

sulphur are given in the following papers by J. N. Gregory [2] and E. B. Greenhill.[3]

RESEARCH GROUP ON THE PHYSICS & CHEMISTRY OF RUBBING SOLIDS,
DEPARTMENT OF PHYSICAL CHEMISTRY,
FREE SCHOOL LANE,
CAMBRIDGE.

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THE LUBRICATION OF METALS BY COMPOUNDS CONTAINING SULPHUR.

By E. B. Greenhill.*

Introduction.

In recent years, a large number of oil-soluble organic compounds containing sulphur have been used as extreme-pressure additives. These compounds, added to mineral oils in concentrations up to 10 per cent have a noticeable effect in preventing the breakdown of the conventional mineral oils under conditions of heavy load and high running temperatures. While many of these compounds prevent deterioration of the oil by acting as anti-oxidants, or as sludge removers, a great number of them are used purely as efficient " boundary " lubricants.

It has generally been assumed that, under extreme conditions, these compounds are decomposed and sulphide films are formed between the surfaces in relative motion. These sulphide films are then able to prevent the occurrence of high wear and seizure in cases where mineral oils would certainly fail. In some cases, the sulphide films are certainly formed, even at room temperatures, as in the case of sulphurized mineral and vegetable oils so frequently used in cutting oils and in drawing fluids, but in other cases where pure compounds such as dibenzyl disulphide are added to gear lubricants the formation of the sulphide film is not obvious.

Many of the substances used as extreme-pressure lubricants are complex mixtures of uncertain composition. This paper describes an attempt to investigate the mechanism of the action of extreme-pressure lubricants using sulphur-containing compounds of known composition and structure.

Experimental.

The apparatus used was that of Bowden and Leben described in previous papers.[1] Steel, copper, cadmium, silver, and platinum surfaces were investigated. The upper slider was made of the same material as the lower plate, so that all results refer to the case where a slider slides on a similar metal plate. All surfaces were thoroughly cleaned before use by the methods described in the previous paper.

The friction was recorded photographically on a moving-drum camera, so that a continuous record of the coefficient of friction was obtained as the temperature of the surfaces was raised. It was usually found that on heating to a sufficiently high temperature, the friction increased sharply to a high value, and at the same time there was a marked increase in the wear and damage of the surfaces. It is clear that a breakdown of the lubricant film

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has occurred; this is referred to as the "breakdown temperature" or transition temperature of the film. This breakdown is usually accompanied by a transition from smooth sliding to "stick-slip" motion. As pointed out by Bowden, Gregory, and Tabor,[2] the point at which breakdown occurs and the type of the motion may depend upon the speed of sliding and the mechanical properties of the system, but for any given conditions it is determined by the nature of the lubricant film.

Results.

Sulphide films.

Thick, visible sulphide films are found to cause a marked reduction in the coefficient of friction between clean metals, though the reduction is never as

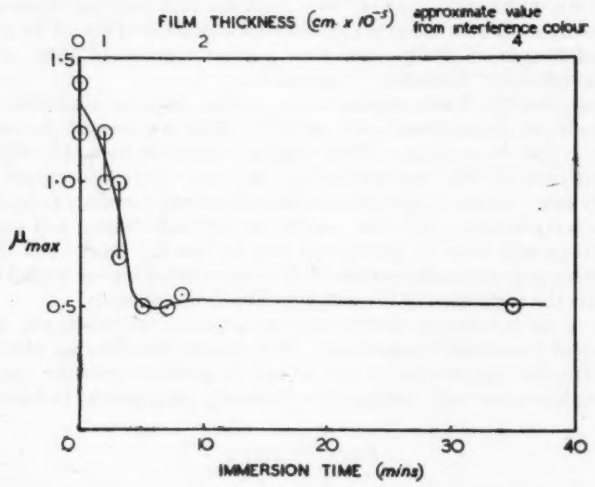


Fig. 1.

VARIATION OF μ WITH THICKNESS OF A SULPHIDE FILM ON COPPER SURFACES.

great as is observed with good boundary lubricants such as the fatty acids. Wear between the surfaces is also reduced as shown by examination of the amount of surface damage during sliding.

The sulphide films were applied in two ways. An ammonium polysulphide solution was used for steel and silver surfaces, while a dilute solution of sodium sulphide was preferable for copper surfaces. The metals were either dipped into the solution for a given period or were merely rubbed with a clean cloth, which had been soaked in the solution. Only the lower plate was treated, the upper contact being always "clean."

The coefficient of friction μ for "clean" steel surfaces varies from 0·7 to 0·9 at room temperature, but a sulphide film showing red/purple interference colours reduces this to a value of 0·50. Thicker films cause no

further reduction, and thinner films, which are scarcely visible, are relatively ineffective. Thick silver-sulphide films give a value of $\mu = 0{\cdot}45$ at room temperatures, rising to 0·70 at 150° C. These values are much lower than those for " clean " silver, which may be greater than 1·50.

Markedly positive results were obtained with copper surfaces. The value of μ for " clean " copper varies from 1·20 to 1·40 at room temperatures, but a sulphide film showing bluish interference colours reduces this to 0·50. Thicker films cause no further reduction, while films showing red interference, or films which are invisible, produce no appreciable reduction. This effect is shown clearly in Fig. 1, which shows the variation of μ with time of immersion in a solution containing 0·40 g of $Na_2S{\cdot}9H_2O$ per litre. The approximate thickness of the film is also indicated. An estimate of the thickness can be made from the interference colours produced, since the equivalent air-film thickness can easily be deduced, and this value is not very different from the actual sulphide-film thickness. (Constable [3] has shown that they are directly proportional.) Figs. 2 and 3 are taper-section photographs produced according to the technique developed by Moore.[4] These are photographs of portions of the tracks produced on the lower plate. Fig. 2 shows the track for clean copper, and Fig. 3 that for copper covered by a sulphide film just thick enough to produce the maximum lowering of the frictional force. The difference in the amount of seizure and tearing, and of the area of work hardening of the surface layers is very apparent.

Other observers have also noted the friction-reducing effect of sulphide films, and have observed a minimum thickness. Hughes and Whittingham,[5] Davey,[6] and more especially Campbell [7] have shown that sulphide films which are sufficiently thick to be visible, lower the friction between copper and steel surfaces. Campbell has plotted similar curves to Fig. 1, and obtains very similar results. When a sulphide film is present, the nature of the sliding is also changed. " Clean " similar metals usually show very irregular sliding with a high friction, whereas sulphide films show a regular " stick-slip " motion of small amplitude.

The effect of adding paraffin oil and a 1 per cent solution of palmitic acid in paraffin oil to the thick sulphide films was also investigated for steel and copper. The addition of paraffin oil to the sulphide film on steel gave results which were better than either paraffin oil or a sulphide film alone. Sliding was never smooth, but the values of μ were quite low, ranging from 0·17 at room temperature to 0·42 at 250° C. Copper surfaces behaved in a similar manner. Campbell [7] and Davey [6] also observed that the addition of paraffin oil resulted in a further lowering of the coefficient of friction.

A 1 per cent solution of palmitic acid on the sulphide films produced very good results. On steel, sliding was quite smooth up to a temperature of 200° C. At this temperature, a rapid transition occurred and the friction rose to a high value. μ varied from 0·10 at room temperature to 0·05 at 200° C. Copper covered by a sulphide film showing blue interference colours also gave good results with a 1 per cent palmitic-acid solution. Sliding was smooth to over 100° C and the friction below 0·10. Above this temperature small " stick-slips " occurred but μ remained low up to 200° C. A 1 per cent solution of palmitic acid on " clean " copper shows a marked

breakdown at approximately 110° C and the friction rises to a high value. This rise is not observed when a sulphide film is first applied to the "clean" surface.

Fig. 4 shows a comparison of these results on steel. Photomicrographs of the tracks produced on the steel plate (Figs. 5, 6, and 7) show the difference in the surface damage during sliding of "clean" steel (Fig. 5), of sulphided steel and paraffin oil (Fig. 6), and of sulphided steel and a 1 per cent solution of palmitic acid in paraffin oil (Fig. 7).

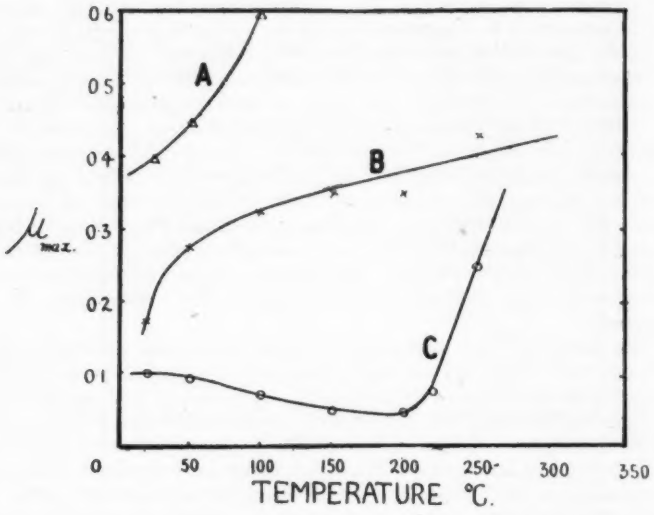


FIG. 4.

VARIATION OF μ WITH TEMPERATURE FOR STEEL SURFACES LUBRICATED WITH:

A. PARAFFIN OIL.
B. " " + SULPHIDE FILM.
C. " " " " + 1 PER CENT PALMITIC ACID.

Long-chain compounds containing sulphur.

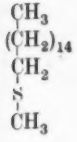
This investigation is restricted to long-chain aliphatic compounds containing sulphur. Such compounds are easily soluble in mineral oil and have a simple structure. Previous work has shown that the most efficient boundary lubricants are those which possess a long carbon chain having a "polar" head, so that similar molecules containing sulphur ought to combine the properties of the fatty acids with the extreme-pressure properties of sulphur. Further, for a fundamental investigation into the action of these extreme-pressure lubricants, the presence of ring structures in the molecule is an added complication to be avoided in the first instance.

The compounds were tested as 1 per cent solutions in pure paraffin oil, unless otherwise specified. Steel, copper, cadmium, platinum, and silver surfaces were used. The lubricant was added to the lower plate approx-

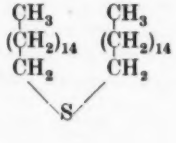
imately 2 minutes before the commencement of the run. In all cases, the frictional behaviour was observed in the range from room temperature up to 250° C.

It was found that none of the compounds tested had any effect on platinum and silver surfaces. The friction remained as high as it was when pure paraffin oil itself was used, but on steel, copper, and cadmium surfaces, it was found that the compounds could be divided into three classes :

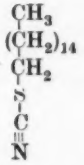
Inactive. Stable sulphur compounds which are not capable of chemical reaction with the metal surfaces are ineffective as boundary lubricants. This group includes sulphides, disulphides, and normal thiocyanates. The following compounds were prepared and found to be inactive on any metal :—



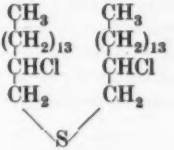
Cetyl methyl sulphide.



Dicetyl sulphide.

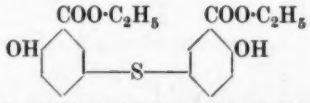


Cetyl thiocyanate.

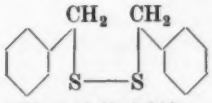


Dichlor-dicetyl sulphide.

Results with these compounds were almost identical with those obtained for pure paraffin oil, with the possible exception of cetyl methyl sulphide, which showed a slight improvement. There was no visible sign of sulphide-film formation even at 200° C. Two commercial additives were also found to fall in the same group. These were :—



Di-(3-carbethoxy-4-hydroxyphenyl) sulphide.



Dibenzyl disulphide.

Again there was no evidence of sulphide-film formation and results were no better than those for paraffin oil itself. All these compounds are relatively stable, and are not decomposed under the conditions of the experiment. The commercial additives are normally used in concentrations of 5 to 10 per cent, so that under very extreme conditions of temperature and pressure, they may give rise to a sulphide film and so behave as extreme-pressure lubricants.

Active. Sulphur compounds which are capable of reaction with a metal surface by replacement of hydrogen are good boundary lubricants on metals like steel, copper, and cadmium, but not on silver or platinum. They therefore resemble the fatty acids which are also inactive on platinum and silver. This group includes mercaptans, sulphonic acids, thio-acids, and the mercapto-acids. Except for the thio-acids, there is little or no evidence for sulphide-film formation, even at 200° C, so that a different mechanism

has to be postulated. The following compounds were prepared and tested :—

$CH_3(CH_2)_{10}CH_2SH$	$CH_3(CH_2)_{14}CH_2SH$	$CH_3(CH_2)_{14}CH_2SO_3H$	$CH_3(CH_2)_{10}CH_2CSSH$	$CH_3(CH_2)_{14}CH_2CSSH$	$CH_3(CH_2)_{13}CH(SH)COOH$
Lauryl mercaptan.	Cetyl mercaptan.	Cetyl sulphonic acid.	Dithiotridecylic acid.*	Dithioheptadecylic acid.*	α-Mercapto-palmitic acid.

All these compounds gave smooth sliding and low friction at room temperature on copper and cadmium surfaces. μ was always below a value of 0·1. On steel surfaces, the friction was somewhat higher, especially with mercaptans, which did not give smooth sliding even at room temperature. As the temperature was raised, a transition to "stick-slip" motion occurred at a characteristic temperature, and the friction rose to a high value. Values of the breakdown temperatures are recorded in Table I. The sulphonic acid was tested as a 1 per cent aqueous solution, since it is insoluble in paraffin oil.

TABLE I.

Breakdown Temperature.

Compound.	Surface.		
	Steel, ° C.	Copper, ° C.	Cadmium, ° C.
Cetyl sulphonic acid . . .	Not definite	125	—
Cetyl mercaptan . . .	20	150	140
Lauryl mercaptan . . .	20	140	—
Dithiotridecylic acid . . .	100	160	—
Dithioheptadecylic acid . .	100	160	—
α-Mercapto-palmitic acid . .	230	290	150

The high breakdown temperatures obtained with α-mercapto-palmitic acid are especially noteworthy. This substance is a very good boundary lubricant, much better than the corresponding fatty acid or mercaptan. The mechanism of the lubrication by these compounds will be discussed later. Figure 8 shows the variation of μ with temperature for some of these compounds on copper surfaces.

Active (not containing a replaceable Hydrogen atom). A third class of compounds was also observed. These compounds do not contain a replaceable hydrogen atom, and do not decompose easily with the liberation of free sulphur. Consequently, there is no obvious possibility of a reaction

* These compounds were prepared by the action of carbon disulphide on the corresponding Grignard reagents. The higher members of this type of compound have not been described in the literature. The compounds were deep red wax-like solids which were far from pure, but fortunately the impurities were chiefly long-chain hydrocarbons which were quite inactive as boundary lubricants. Some samples were purified by saponification.

between the compounds and the metal surfaces. This class includes the xanthates and certain dithiocyanates.

Cetyl ethyl xanthate, $CH_3—(CH_2)_{14}—CH_2—S—C\langle^{S}_{OC_2H_5}$

gave good results on copper and cadmium surfaces. The transition on copper occurred at 150° C and at 120° C on cadmium. There was no evidence of sulphide staining. However, it was shown that copper powder reacts with the xanthate to form a green compound at 100° C. The nature of this compound is unknown.

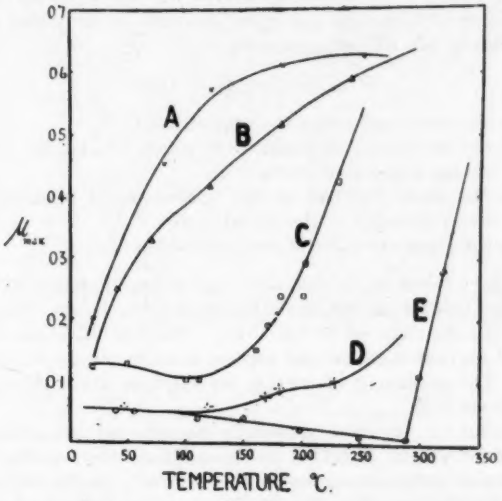


FIG. 8.

VARIATION OF μ WITH TEMPERATURE FOR COPPER SURFACES LUBRICATED WITH :

A. PURE PARAFFIN OIL.
B. ,, ,, ,, + 1 PER CENT CETYL SULPHIDE.
C. ,, ,, ,, + 1 PER CENT CETYL METHYL SULPHIDE.
D. ,, ,, ,, + 1 PER CENT CETYL MERCAPTAN.
E. ,, ,, ,, + 1 PER CENT α-MERCAPTO-PALMITIC ACID.

The work of de Kadt [8] has shown that compounds which contain two thiocyanate groups adjacent to one another are very effective, especially when a carboxylic-acid group is also present. For example, dithiocyanostearic acid, prepared from oleic acid and free thiocyanogen, is an excellent boundary lubricant on steel. The transition occurs above 300° C. A compound prepared from 1 : hexadecene and thiocyanogen is almost as good. The behaviour of these compounds is obviously not due to sulphide-film formation. The evidence points to the formation of a film of ferric thiocyanate.

DISCUSSION.

In the first section of this paper, it is shown that sulphide films are able to reduce the friction between sliding metals, provided they are above a

critical thickness. Taper-section photographs of copper surfaces show that the wear and seizure due to sliding are very much reduced. This is due to the fact that the amount of intimate metallic contact known to occur during lubricated sliding to some extent is very much less than when "clean" metals are used. In other words, the sulphide film reduces the amount of local welding during sliding, and so may be called an anti-welding film. The frictional force may, however, be considerable compared with efficient boundary lubricants such as the fatty acids. This can be understood clearly if we consider the formula recently proposed by Bowden, Gregory, and Tabor.[2] They postulate that the frictional force F during lubricated sliding is related to the shear strength of the metal and of the lubricating film in the following manner:—

$$F = A(\alpha s_m + (1 - \alpha)s)$$

where A is the area supporting the applied load,
α is the fraction of this area over which breakdown of the lubricating film has occurred.
s_m is the shear strength of the welded metal junctions, *i.e.*, the shear strength of the metal,
and s is the shear strength of the lubricating film.

A good boundary lubricant is able to reduce α considerably, and the shear strength of the film (soap in the case of the fatty acids) is low. Consequently μ is very low (of the order of 0·05 to 0·10). Sulphide films also reduce α to a large extent, so that the wear and surface damage is reduced, but s is still fairly high. The coefficient of friction for sulphide films, therefore, never falls below about 0·50.

When paraffin oil, or more especially paraffin oil containing a small proportion of fatty acid, is added to the sulphide film, results indicate a further noticeable reduction in the frictional force. In the latter case, α is also reduced by the boundary film of chemi-sorbed fatty acid (metal-soap film) formed on top of the sulphide film, and so the friction is very low. Further, the presence of the sulphide film prevents excessive wear and seizure when the boundary film of metal soap breaks down (*i.e.*, softens or dissolves into the superincumbent oil; see Bowden, Gregory, and Tabor [2]).

It is probable that this mechanism accounts for the effect of the majority of extreme-pressure lubricants containing sulphur. Sulphurized lubricants, such as sulphurized mineral oils or fatty oils, form a visible sulphide stain even at room temperatures, while stable compounds like dibenzyldisulphide will give rise to a sulphide film at high temperatures and pressures, especially in concentrations of up to 10 per cent in mineral oils. The work of Simard, Russel, and Nelson [9] has demonstrated the formation of sulphide films on certain metals when a lubricant containing lead naphthenate and free sulphur is used. Clark, Gallo, and Lincoln,[10] using a sulphurized lubricant prepared from radio-active sulphur, have observed the formation of a radio-active film. Further support for the above mechanism comes from the results obtained with sulphurized lubricants on the Bowden–Leben apparatus. Sulphurized oleic acid, prepared either from free sulphur or from sulphur chloride, is a very effective boundary lubricant up to temperatures over 300° C. A visible sulphide film is formed. Sulphurized cetene

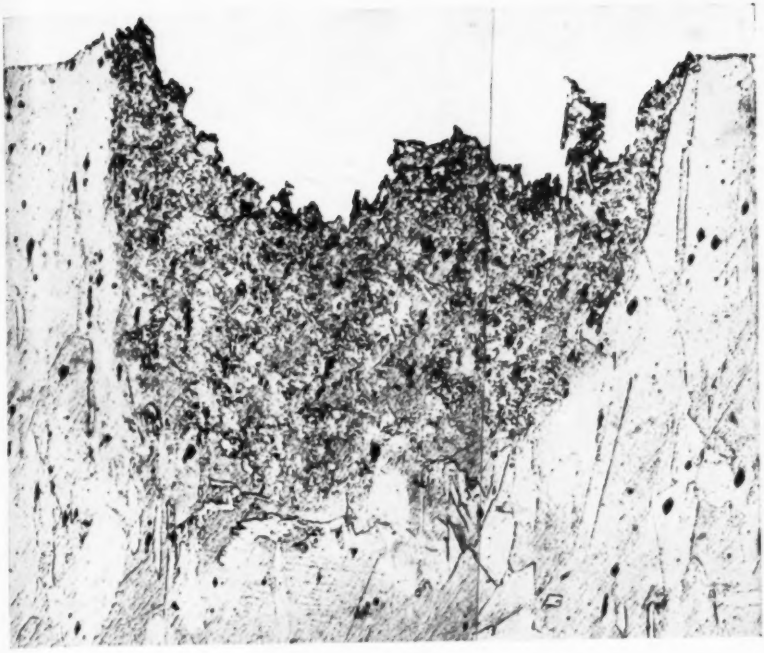


FIG. 2.

TAPER SECTION OF A TRACK PRODUCED WHEN A COPPER SLIDER SLIDES ON A COPPER PLATE UNDER " CLEAN " CONDITIONS. NOTE THE CONSIDERABLE DEPTH OF THE WORK-HARDENED AREA. (HORIZONTAL, $\times 150$; VERTICAL, $\times 1500$)

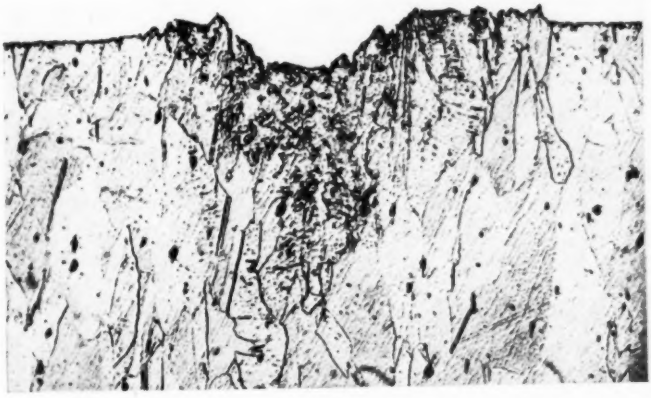


FIG. 3.

TAPER SECTION OF A TRACK PRODUCED WHEN A COPPER SLIDER SLIDES ON A COPPER PLATE COVERED WITH A SULPHIDE FILM JUST THICK ENOUGH TO PRODUCE THE MAXIMUM LOWERING IN THE COEFFICIENT OF FRICTION. (HORIZONTAL, $\times 150$; VERTICAL, $\times 1500$.)

[*To face p.* 666.

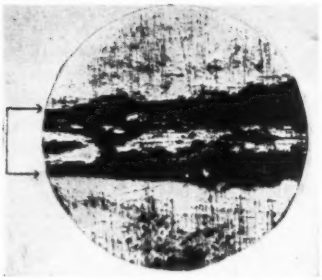


FIG. 5.

MICROPHOTOGRAPH OF TRACK PRODUCED WHEN A STEEL SLIDER SLIDES ON A "CLEAN" STEEL SURFACE. (× 30.)

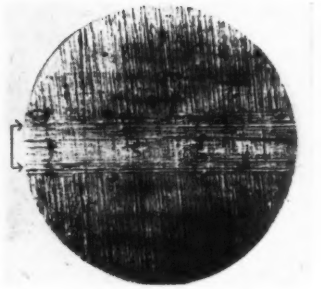


FIG. 6.

MICROPHOTOGRAPH OF TRACK PRODUCED ON A STEEL SURFACE LUBRICATED BY A SULPHIDE FILM WITH PARAFFIN OIL. (× 30.)

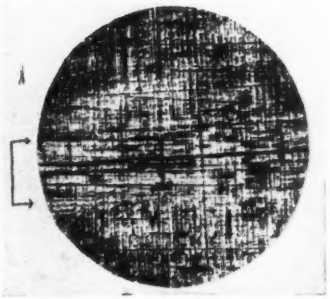


FIG. 7.

MICROPHOTOGRAPH OF TRACK PRODUCED ON A STEEL SURFACE LUBRICATED BY A SULPHIDE FILM COVERED BY A 1 PER CENT SOLUTION OF PALMITIC ACID IN PARAFFIN OIL. (× 30.)

is also effective. But many relatively stable sulphur compounds may be good boundary lubricants for an entirely different reason.

Sulphur Compounds.

We have seen that the sulphur compounds tested in this investigation fall into three classes. The first class of compounds includes the sulphides and disulphides which are inactive under the conditions of the experiments. They do not give rise to a sulphide film, and do not lubricate any metal.

The second class consists of compounds which are acidic in nature, and which are capable of reaction with a metal to form substances analagous to metal soaps. They are all effective boundary lubricants, but do not form any visible sulphide film (with the exception of the thio-acids, which are very unstable). They are, however, completely inactive on such metals as platinum and silver. The resemblance to the fatty acids is therefore apparent. Bowden, Gregory, and Tabor [2] have shown that fatty acids do not lubricate those metals with which they do not react. They find that the breakdown temperature observed when a metal is lubricated by a fatty acid depends not only on the acid but also on the metal. The evidence suggests that a fatty acid attacks the metal surface or its oxide film, and gives rise to a very thin layer (probably a monolayer) of chemi-sorbed metallic soap. This soap film is able to function as a very efficient boundary lubricant. In our previous equation, α is very much reduced, and s, the shear strength of the soap, is low. Such films lubricate up to temperatures which are often very close to the bulk softening point of the soap. Electron-diffraction investigations, and experiments on the lubrication of metals by mono- and multi-layers of fatty acids and their metallic soaps, have all tended to support this view.

It seems likely that a similar mechanism applies to the sulphur compounds in Class 2. Mercaptans are much more acidic than the corresponding alcohols (which are poor lubricants) and are known to react with certain metals. The other compounds all contain hydrogen atoms which are easily replaceable by a metal. This view is further supported by experiments which were carried out with the metal soaps themselves. The copper and cadmium soaps of cetyl mercaptan and of α-mercapto-palmitic acid can be readily prepared by the usual precipitation methods. If these soaps are applied as thick films to non-reactive surfaces, such as platinum, by evaporation from solution in alcohol or ether, it is found that they lubricate readily. The coefficient of friction μ is of the same order as that observed when the free " acids " are used on the appropriate " reactive " metal, and further, these films lubricate up to temperatures not far removed from the break-down temperatures observed on the " reactive " metals.

Experiments using paraffin-oil solutions of the metal soaps on various metals also support the view that formation of a metal-soap monolayer occurs at the metal surface when the free acids are used.

It is likely, then, that the sulphur compounds in Class 2 do behave in a similar manner to the fatty acids. This is true whatever the nature of the changes occurring at the breakdown temperature, which, however, does correspond roughly to the bulk softening point of the metal soaps. Certainly, the softening point of the soap is one of the most important factors causing breakdown.

The third class of compounds—those which do not have any replaceable hydrogen atoms, and which do not form visible sulphide films, seem to form an exception to the idea that chemical reaction is necessary for boundary or extreme-pressure lubrication. But it was found that cetyl-ethyl xanthate readily attacked copper powder at 100° C to form a green soap-like material of unknown structure. The xanthates therefore fall into Class 2.

The di-thiocyanates, however, are more difficult to explain. Normal mono-thiocyanates are very stable and inactive as lubricants, and it was suspected that these di-thiocyanates might give rise to free thiocyanogen at elevated temperatures. They are only effective on steel surfaces, and a reddish stain was often noticed after the experiments. Consequently, some experiments were carried out on ferric thiocyanate films. Ferric thiocyanate films deposited on steel surfaces by evaporation from an ether solution were found to be effective boundary lubricants in the absence of moisture which causes rapid hydrolysis. If a solution of free thiocyanogen in ether is added to some paraffin oil and placed on a steel surface, the ether soon evaporates, leaving a visible red film of ferric thiocyanate covered by paraffin oil which prevents hydrolysis. Under these conditions, smooth sliding and a low friction is obtained up to temperatures above 200° C. Ferric thiocyanate is therefore a good boundary lubricant under anhydrous conditions, and resembles ferric chloride closely. It would seem that these di-thiocyanates function in a manner exactly analogous to the extreme-pressure lubricants containing chlorine.

Conclusion.

These results support the view that all extreme-pressure lubricants function as a result of chemical reaction with the moving surfaces. Extreme-pressure lubrication, in fact, becomes a problem in controlled corrosion. The stability of the additive has to be so chosen that the corrosion does not become excessive under conditions which are likely to occur in any particular case.

It is not suggested that the compounds studied in this paper are necessarily good extreme-pressure additives, but that the mechanism of extreme-pressure lubrication for these compounds corresponds to that which actually occurs with conventional additives in practice. Finally, it is to be pointed out that many extreme-pressure additives are specific for a given metal or group of metals, so that the problem of choosing an extreme-pressure additive depends not only on the conditions such as temperature and pressure, but also on the type of metal to be lubricated. It is clear, too, that the stability of the additive which can be tolerated depends entirely on the conditions which will prevail at the moving surfaces. Obviously one may choose a very unstable compound for such operations as cutting and drawing, since the corrosion problem is not important. But in a running engine, an additive which is too unstable under running conditions will do more harm than good, mainly as a result of excessive chemical corrosion. What is required is an additive which will give rise to chemical reaction only at temperatures or pressures in the danger zone, *i.e.*, when welding and tearing become so great that high wear and subsequent seizure occur.

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THE LUBRICATION OF METALS BY COMPOUNDS CONTAINING CHLORINE.

By J. N. Gregory.*

Introduction.

Many organic compounds containing chlorine have been used in recent years as extreme-pressure additives for mineral oils, thereby making possible lubrication under extreme conditions of pressure and temperature. The frictional force between the moving parts was considerably reduced and extensive wear and ultimate seizure were avoided. The patent literature covering the development in this field of extreme-pressure lubrication over the last ten or fifteen years is voluminous, and there would appear to be no clear correlation between the type of compound used and its effectiveness as an additive, and little data to show the mechanism by which these compounds act. The general opinion seems to point to the formation of a chloride film between the metal surfaces, owing to the thermal decomposition of the additive during running. It would appear that this chloride film is able to protect the surface to a considerable extent under conditions where the conventional lubricant would certainly fail. Few workers in the field have, however, offered evidence to show that this theory is tenable, or to explain why a chloride film is capable of functioning in this manner.

Hughes and Whittingham [1] showed in 1942 that many types of surface film considerably reduced the frictional force between sliding metals, and that chloride films formed by immersion of copper in hydrochloric acid did behave in this manner.

Davey,[2] working with the four-ball machine, describes tests on several simple organic chlorides, and suggests that chloride films are formed by the release of " atomic " chlorine as a result of decomposition. Compounds which are not saturated with chlorine are not effective, because hydrochloric acid is liberated. According to this view, the molecule should be saturated with chlorine, which becomes labile in extreme use.

This paper deals with the lubricating properties of artificially produced chloride films, and of certain organic compounds containing chlorine which decompose at elevated temperatures in a known manner.

Experimental.

Apparatus.

The apparatus of Bowden and Leben, fully described in previous papers,[3] was used throughout this investigation. The upper sliding contact was always made of the same metal as the lower plate, and before use was well polished in a chuck with 600 emery paper. The lower flat plate was ground

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under water on a well-worn 220 emery paper, and dried either in acetone–*iso*propyl ether vapour (steel), or by air drying after immersion in boiling water (copper, cadmium, and platinum). Steel surfaces were treated with rouge and sodium hydroxide solution before drying. In all experiments, the load applied between the surfaces was 4000 g, and the speed of sliding was 0·01 cm/sec. Under these conditions, fluid lubrication was impossible, and the lubricants were therefore tested under " boundary " conditions.

The Friction of Artificially Produced Chloride Films.

Frictional experiments were carried out on chloride films produced by exposing steel, copper, and cadmium surfaces to dry chlorine gas for a definite period. In the case of steel and platinum surfaces, anhydrous ferric chloride was deposited on the surface by evaporation from an ether solution.

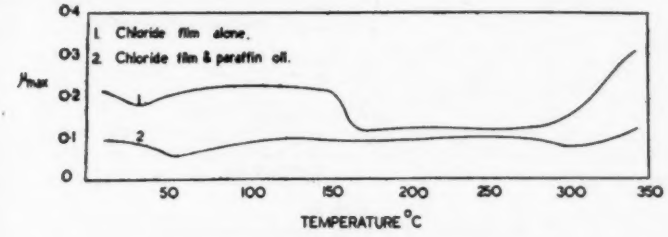


FIG. 1.

VARIATION OF μ WITH TEMPERATURE FOR STEEL SURFACES LUBRICATED BY CHLORIDE FILMS.

Fig. 1 shows the variation of the coefficient of friction (μ) with temperature for chloride films on mild-steel surfaces. In this experiment, the lower steel plate was exposed to chlorine gas for 30 minutes, and the chloride film was sufficiently thick to produce faint reddish interference colours. With the least delay possible (to prevent hydrolysis of the film by atmospheric moisture) frictional tests were carried out on the surface, alone, and covered with paraffin oil. In both cases, the sliding was smooth and the friction low, up to temperatures over 300° C. The addition of the paraffin oil resulted in a slightly lower value of μ than that observed with the dry surfaces.

Ferric-chloride films deposited on steel from ether solution gave almost identical results, but if deposited on platinum in this way, the lubrication was very poor. This can be seen in Fig. 2.

Chloride films obtained by exposing copper and cadmium surfaces were also effective in lowering the frictional force below that observed with the "clean" metals. Exposed copper surfaces had a value of $\mu = 0{\cdot}3$ rising to 0·4 at 350° C when dry, while the addition of paraffin oil resulted in a value of $\mu = 0{\cdot}2$ over the whole temperature range. The friction coefficient of " clean " copper is over 1·0.

Cadmium surfaces showed a value of $\mu = 0{\cdot}2$ to 0·3 when exposed to chlorine and then covered with paraffin oil—a value much lower than was observed when " clean " cadmium surfaces were covered with paraffin oil.

Chloride films on steel surfaces were very readily hydrolysed by the presence of moisture in the air, and rapidly lost all their lubricating properties if special precautions were not taken. The films were formed in a desiccator, and were tested immediately after removal.

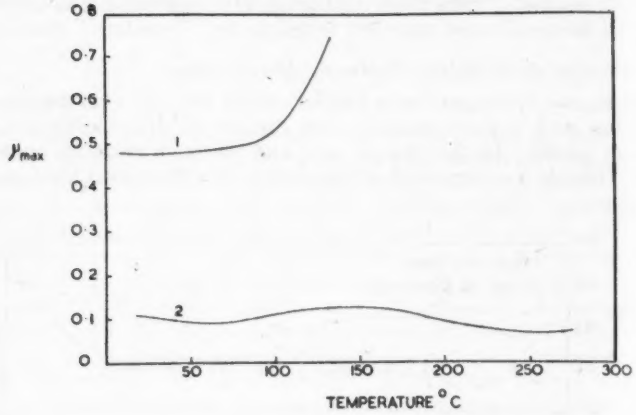


FIG. 2.

VARIATION OF μ WITH TEMPERATURE FOR:

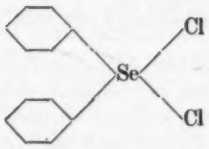
1. PLATINUM SURFACES LUBRICATED BY ANHYDROUS FERRIC CHLORIDE DEPOSITED FROM AN ETHER SOLUTION.
2. MILD-STEEL SURFACES SIMILARLY LUBRICATED (BOTH SURFACES COVERED WITH PARAFFIN OIL).

Frictional Tests with Compounds Containing Chlorine.

Long-chain organic halides. Octadecyl chloride, either pure or in solution, is a relatively poor lubricant for steel surfaces, although results show that the behaviour may be considerably better than paraffin oil. The pure substance gave "stick-slip" sliding over the whole temperature range from 20° to 200° C as was observed with paraffin oil, but the coefficient of friction was about 0·15 at 20° C, and rose to 0·30 at 200° C, as compared with a minimum value of 0·40 observed with paraffin oil. Although this slight improvement was observed, it is obvious that the results are very much poorer than those for the chloride films, so that it seems unlikely that any chloride film is formed, the substance being too stable under the test conditions. Probably the slight improvement is a result of physical adsorption at the metal surface, of the strongly dipolar molecular. If, however, octadecyl chloride was tested below 20° C, that is, below its melting point, a very low friction with smooth sliding resulted. Cetyl bromide, cetyl iodide, and cetyl thiocyanate behaved in a similar manner.

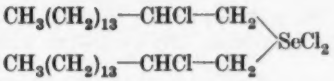
Compounds containing the $SeCl_2$ group. Early in this investigation, it was found that selenium compounds which contained the $SeCl_2$ group were very effective as boundary lubricants. The first of these—diphenyl selenium dichloride, when tested as a 1 per cent suspension in paraffin oil,

caused a very marked drop in the coefficient of friction between steel surfaces at approximately 70° C. Smooth sliding and low friction ($\mu = 0{\cdot}06$)



persisted from 70° C to over 300° C. Suspensions which were even more dilute still showed a similar behaviour. Below 70° C the frictional behaviour was similar to paraffin oil itself, and gave " stick-slip " sliding with a relatively high friction. This compound, however, suffers from the disadvantage of being insoluble in mineral oils, and other similar compounds were prepared, which were freely soluble.

ββ′-dichlor-dicetyl selenium dichloride,



prepared by the reaction of 1 : 2-hexadecene with selenium tetrachloride, is readily soluble in paraffin oil, and shows similar lubricating properties

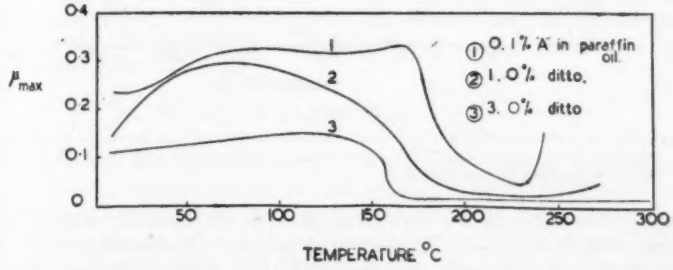


FIG. 3.

VARIATION OF μ WITH TEMPERATURE FOR STEEL SURFACES LUBRICATED BY PARAFFIN-OIL SOLUTIONS OF ββ′-DICHLOR-DICETYL SELENIUM DICHLORIDE (" A ").

to the diphenyl compound. Fig. 3 shows the variation of μ with temperature with concentrations from 0·1 to 3 per cent in paraffin oil on mild-steel surfaces. (The compound is referred to as *A* in the figure for convenience.) At room temperatures, small stick-slips were observed with μ varying from 0·1 for 3 per cent to 0·2 for 1 per cent solutions. On heating the surfaces, the friction showed a slight rise at first, followed by a sharp drop at 160° to 180° C. From this temperature to 300° C, the motion was smooth, and the friction very low ($\mu = 0{\cdot}01$—$0{\cdot}03$). A 0·1 per cent solution in paraffin oil also showed the marked decrease in friction at 160° to 180° C, but further temperature increase caused a rapid rise again.

It is well known that paraffin-oil solutions of fatty acids such as stearic acid, on mild-steel surfaces, give smooth sliding and low values of μ from

room temperatures to 130° to 160° C, so that a mixture of this acid plus the compound *A* dissolved in the oil should give smooth sliding and low friction from room temperatures up to over 300° C. Fig. 4 shows this to be the case for paraffin oil containing 1 per cent stearic acid and 1 per cent of *A*.

The compound *A* was also tested on copper and cadmium surfaces. With copper, a 3 per cent solution gave smooth sliding to 100° C followed by a transition to irregular sliding and high friction. Cadmium surfaces showed poor lubrication over 40° C. In both cases, the results were better than for paraffin oil alone, but anything approaching the extremely good lubrication with steel surfaces was quite absent.

Another oil-soluble selenium compound containing the $SeCl_2$ group is di-(1-hydroxy-2-carbomethoxy-phenyl)-4 selenium dichloride, prepared according to the method of Nelson *et al* [4] by reaction of methyl salicylate with selenium oxychloride. Two per cent of this compound in paraffin oil again showed a characteristic drop in the value of μ when tested on steel surfaces. In this case, the transition occurred at 130° to 140° C. It is interesting to note the removal of the chlorine of the $SeCl_2$ group completely eliminates the transition. By hydrolysis with sodium-bicarbonate

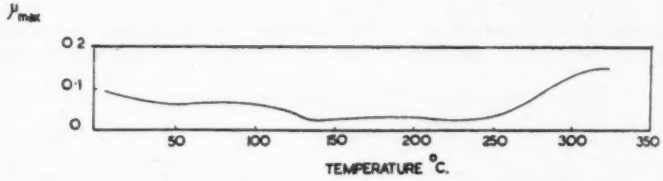


FIG. 4.

VARIATION OF μ WITH TEMPERATURE FOR STEEL SURFACES LUBRICATED BY A PARAFFIN-OIL SOLUTION CONTAINING 1 PER CENT STEARIC ACID AND 1 PER CENT $\beta\beta'$-DICHLORDICETYL SELENIUM DICHLORIDE.

solution, the compound is converted into the dihydroxide, while if it is heated with zinc dust, dechlorination occurs, and the selenide results. No drop in the value of μ was observed with these compounds, and they are poor boundary lubricants.

Long-chain acid chlorides. A few experiments were carried out with dilute stearyl chloride solutions. On steel surfaces, low friction and smooth sliding was observed up to 300° C, but copper surfaces were not lubricated. A solution containing 0·5 per cent was sufficient on steel.

DISCUSSION.

Chloride films have been shown to be very efficient boundary lubricants on steel surfaces, both when dry and when in the presence of paraffin oil. They are not very effective on copper or on cadmium surfaces. On steel surfaces, a thin film of iron chloride causes a great reduction in the frictional force between the " clean " metals and in the amount of wear and seizure. This can only mean that the " welded " junctions, which form between the metals at points of intimate contact, are greatly reduced in number. The

shear strength of the film is also low, so that friction and wear are greatly reduced. Such films are, however, only effective when they are anhydrous. Hydrolysis due to moisture causes a rapid rise in the coefficient of friction, and the lubricating properties of the film become poor.

The lubricating properties of organic compounds containing chlorine vary with the stability of the compounds. Long-chain halides, such as octadecyl chloride, are stable even at 300° C, so that no chloride film is formed, and these compounds are relatively poor lubricants. On the other hand, compounds containing relatively unstable chlorine atoms, which may become labile at moderate temperatures, are efficient lubricants. The properties of the compounds containing the $SeCl_2$ group seem to be wholly dependent on the chlorine atoms and not on the selenium. This is shown by hydrolysis or dechlorination. If the chlorine is removed by either method, the lubricating properties disappear. Further, the frictional properties depend entirely on the formation of a chloride film at a temperature characteristic of any one compound. The formation of this film can actually be observed, and the drop in the coefficient of friction occurs just at this temperature. In other words, the chlorine in the $SeCl_2$ group is "ionizable" (as is shown by silver-nitrate precipitation from an alcohol–ether solution) and readily forms a chloride film on the metal surface, provided the temperature is above a certain value.

Further direct evidence of the formation of a chloride film on iron surfaces was obtained by refluxing iron filings with an alcoholic solution of diphenyl selenium dichloride. After reaction, it was found that iron chloride had been formed, and diphenyl selenide was recovered as a yellow oil. The reaction therefore is as follows :—

$$Ph_2SeCl_2 + Fe \longrightarrow FeCl_2 + Ph_2Se$$

Titration of the iron chloride formed, in aqueous solution, showed that 75 per cent was ferrous chloride and the remainder ferric chloride.

Once the chloride film has been formed on the surface, the similarity of the friction tests to those with artificially produced iron-chloride films, makes it quite obvious that the chloride film is responsible for the efficient lubrication. But it is not clear whether the film is ferric or ferrous chloride, or even an oxychloride. Chemical tests indicated that anhydrous ferrous chloride was produced from the $SeCl_2$ compounds, and it is possible that the film formed by exposing steel to chlorine may be ferrous chloride, at least at higher temperatures, where the reaction $2FeCl_3 + Fe \longrightarrow 3FeCl_2$ could occur. Also, anhydrous ferric chloride sublimes at 285° C and would therefore be removed from the surface above this temperature. Friction tests indicate that the film is stable, to at least 300° C. The presence of the superincumbent paraffin oil may, however, complicate the removal of the film. The composition of the lubricating layer, therefore, is not exactly known.

Anhydrous chloride films are undoubtedly produced on copper and cadmium by these compounds also, but, as indicated by experiments on artificial chloride films, they are unable to function as efficient boundary lubricants. Tests indicate that they do have some effect, since the results are always very much better than those with paraffin oil alone.

Conclusion.

It has been shown that compounds containing reactive chlorine atoms under certain circumstances (*i.e.*, moderate heating) can produce on steel surfaces a film of iron chloride which has extremely good frictional properties, and which will maintain these properties to very high temperatures. The lubricating films are only stable in the absence of moisture.

It is not suggested that the compounds mentioned in this paper are necessarily good "extreme-pressure lubricants." Some of them are too unstable, and corrosive, for practical use. But it is suggested that conventional chlorine-containing extreme-pressure lubricants may function in a similar manner. The formation of the chloride film takes place under extreme conditions of temperature and pressure, due to decomposition of the compound with the liberation of "active" chlorine, and these films are formed at the point where conventional mineral-oil lubricants fail. The problem of making a good "extreme-pressure additive" therefore reduces itself to choosing a compound which will give rise to a protective film under extreme conditions, but which is sufficiently stable and non-corrosive under less severe conditions.

Two other points of interest also emerge from these experiments. First, the film should be anhydrous and the formation of hydrochloric acid is to be avoided. This is desirable from the corrosion point of view, in addition to the lubricating properties.

Secondly, chlorine-containing additives may be specified for steel and ferrous alloys, and the use of such additives for other metals may not give very beneficial results. In the case of ferrous alloys, combination of a chlorine additive with a fatty material may be beneficial in certain cases.

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[3] Bowden, F. P., and Leben, L. *Proc. Roy. Soc.*, 1939, *A* **169**, 371.
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ALKYLNAPHTHALENES. PART II.* THE METHYL, ETHYL, AND *N*-PROPYL NAPHTHALENES.

By S. H. Morrell,† G. B. Pickering,† and J. C. Smith.†

The memoirs comprising this series will describe the preparation and purification of a number of alkylnaphthalenes, and in this paper are recorded the freezing points, boiling points, and refractive indices of the first three members of the homologous mono-*n*-alkylnaphthalenes, both of the α- and of the β-series. (See Table I.)

All the simple mono-*n*-alkylnaphthalenes, with the exception of 2-methylnaphthalene, are liquids at the ordinary temperature and, as solid derivatives of these hydrocarbons, the picrates are usually prepared. With the methyl and ethyl naphthalenes no difficulty arises; for the *n*-propyl homologues, however, not only have there been no data on the freezing points of the hydrocarbons, but also there is a large discrepancy in the recorded values for the melting point of the picrate of 1-*n*-propylnaphthalene.[2, 3]

The purification of the β-compounds presents few difficulties since, almost invariably with the substituted naphthalenes, the β-compounds are higher-melting and less soluble than the α-isomerides. In contrast, however, the picrates of some of the α-acylnaphthalenes are less soluble than those of the β-isomerides and can be completely purified; decomposition affords the pure α-acyl- and hence the pure α-alkylnaphthalenes are obtained by reduction.

Specimens of 1-*n*-propylnaphthalene having identical physical constants have now been obtained by two different routes, but afford unstable picrates which melt at 84° to 87°. Investigation of the binary system, 1-*n*-propylnaphthalene–picric acid, reveals the formation of a 1 : 1-compound with a non-congruent melting point. The styphnates of the *n*-alkylnaphthalenes are even less stable than the picrates, those from 1- and 2-ethylnaphthalene showing some decomposition near the melting point and those of the *n*-propylnaphthalenes being unobtainable. The 1 : 3 : 5-trinitrobenzene complexes, on the other hand, are stable and are recommended as solid derivatives for the identification of these liquid hydrocarbons.

Comment on the changes in physical constants during the ascent of the homologues series will be possible when further members have been studied.

1-Methylnaphthalene.

Because of its low melting point (−31°) and of the formation of solid solutions with the chief impurity (2-methylnaphthalene) the 1-methylisomeride is difficult to purify.

Morgan and Coulson [4] surveyed the previous work on the isolation of the methylnaphthalenes and concluded that some of the earlier samples of

* "The Ten Dimethylnaphthalenes" [1] is regarded as Part I of this series.

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TABLE I.

n-Alkylnaphthalenes.

Alkyl naphthalene.	M. pt., ° C.	B. pt. ° C/760 mm.	n_D^{20}.	Styphnate, m. pt., ° C.	Picrate, m. pt., ° C.	T.N.B., complex m. pt., ° C.
1-Methyl	−31 to −30	244·5	1·6174	134–135	141·5	153·5–154·5
			n_D^{25} 1·6149		141 [5]	147 [15]
			n_D^{40} 1·6070		141 [6]	
	−30·77 [7]	244·78 [7]	n_D^{20} (1·6175) [7]		141–142 [16]	
			n_D^{25} 1·6149 [7]			
	−31 [8,9]	244–245 [8,9]	1·6167 [8,9]			
	−31 [17]	244·4 [17]	1·6172 [17]			
2-Methyl	34·2	241	(1·6121)	129·5	116–117	124
	34 [8,9]		n_D^{40} 1·6017		115·8 [6]	123 [16]
	34·44 [7]	241·14 [7]	n_D^{40} 1·6019 [7]			
	34·5 [17]		n_D^{40} 1·6015 [17]			
	35·1 [10]		n_D^{50} 1·5965 [17]			
			n_D^{40} 1·6028 [10]			
1-Ethyl	−13·5	259	1·6062	111–113 (dec.)	99	112
		136/18 mm				
		257–259 [21]			98 [21]	
	−15 [25]	256/756 mm [26]	$n_D^{14.2}$ 1·6089 [25]		98·5 [25]	
			1·6075 [26]			
2-Ethyl	− 7	258	1·5999	88–90 (dec.)	77	87–88
	−7·5 to −6·5 [25]	257–258 [25]	n_D^{15} 1·6028 [25]		76·5–77 [25]	
	−19 [53]	248–253 [53]	n_D^{25} 1·591 [53]		75–76 [54]	
		117–118/10 mm [52]			72–73 [52]	
1-*n*-Propyl	−13 to −12	272–273	1·5923	—	84–86 (dec.)	86–87
	and −9	133–135/10 mm			and 73	
		274–275 [2]			141–142 [2]	
		275–276 [3]			92 [3]	
2-*n*-Propyl	−3	273–274	1·5872	—	90	99
		277–279 [2]			90–92 [2]	

Data without superscripts are those obtained in this investigation; (dec.) indicates that the compound decomposes near the m. pt.; ( ) denotes a value obtained by extrapolation.

1-methylnaphthalene were probably the eutectic mixture (m. pt. −47°) containing 17·5 per cent of the 2-methyl-isomeride.

On sulphonation 1-methylnaphthalene readily yields 1-methylnaphthalene-4-sulphonic acid, which is sparingly soluble in 30 to 50 per cent sulphuric acid; the 2-methyl-isomeride yields the 1-, the 8-, or the 6-sulphonic acid. Making use of these facts Morgan and Coulson [4] separated 1-methylnaphthalene-4-sulphonic acid from a fraction of tar oil (from which much 2-methylnaphthalene had been frozen out), recrystallized it and then regenerated the hydrocarbon by desulphonation with superheated steam. Their specimen melted at −33° to −32°.

Cosciug [5] and also Morgan and Coulson [4] attempted to separate the two isomers by fractional crystallization from alcohol of the mixed picrates, but failed. As was shown by R. and W. Meyer [6] the melting point changes only slowly for the picrates containing less than 60 per cent of the 1-isomeride. (The picrate of 1-methylnaphthalene melts at 141·5° and that of 2-methylnaphthalene at 116°.) Meyer and Meyer,[6, p. 1251] give a diagram in which some of the points are freezing points and others are melting points of mixtures of the two picrates. In this diagram there is some indication of a 1 : 1 "compound," m. pt. 121° to 123°, between the picrates. The formation of such a "compound" would explain the frequent production of a "picrate melting at 121° to 123°" from impure samples of 1- and 2-methylnaphthalene.

With the advent of efficient fractionating columns it became possible to separate, by distillation alone, isomerides the boiling points of which differed by only 3° to 4°. Mair and Streiff [7] at the Bureau of Standards used a column 280 by 2·5 cm and equivalent to 100 theoretical plates to separate the constituents of a kerosine fraction of Oklahoma petroleum. Fractions of b. pt. 145° to 146·5°/56 mm solidified at room temperature and were mainly 2-methylnaphthalene; fractions consisting of the eutectic mixture (approx. 82·5 per cent 1-Me, m. pt. −47°) distilled at 148·3°, and lastly at 148·9°/56 mm a specimen of m. pt. −31·9° was collected. Further fractionation of this last fraction gave a product of m. pt. −31·0° which, recrystallized from ethyl alcohol, gave 1-methylnaphthalene of m. pt. −30·90°; b. pt. 244·78°/760 mm. By extrapolation they arrived at −30·77° ±0·06° as the m. pt. of pure 1-methylnaphthalene.

E. A. Coulson [8, 9] maintained that the chemical method of separating the methylnaphthalenes would generally be more expedient. After the first fractional distillation of tar oil he removed basic substances by shaking with 60 per cent sulphuric acid. Instead of removing the 2-methylnaphthalene by crystallization (cooling nearly to the eutectic temperature) he removed some at −15° and then concentrated the 1-methylisomeride by sulphonation followed by fractional desulphonation. For this purpose the mixed sulphonation product was diluted until its boiling point was about 120° and then boiled while steam at 115° to 124° was passed through. The distillate yielded 78 to 80 per cent 1-methylnaphthalene (free from paraffins); at higher temperatures the sulphonic acids from the 2-isomeride were desulphonated. When this product containing 78 to 80 per cent of the 1-methyl-isomeride was sulphonated and the reaction mixture diluted and cooled, it deposited 1-methylnaphthalene-4-sulphonic acid in a form readily filtered and then recrystallized from 35 per cent sulphuric acid.

Data without superscripts are those obtained in this investigation; (dec.) indicates that the compound decomposes near the m. pt.; ( ) denotes a value obtained by extrapolation.

Coulson [9] thus obtained a specimen, m. pt. −34° to −31° (99 per cent 1-Me). Using a specimen of m. pt. −31° and 2-methylnaphthalene of m. pt. 34° he investigated the binary system.[8]

In the present authors' experience there appeared to be one sulphonic acid *not* derived from 1-methylnaphthalene which decomposed at 124°, thus making the earliest fractions of the desulphonated material rather impure. It was found, however, after several trials, that if the sulphonation even of the crude oil containing only 60 to 70 per cent of the 1-methyl-isomeride was carried out rapidly at 5° to 25° instead of slowly at 0° to 20°, the 1-methyl-naphthalene-4-sulphonic acid separated easily; the fractional desulphonation followed by resulphonation could then be omitted. The authors are much indebted to Dr Coulson for advice and help in the use of his process and also to the Director of the Chemical Research Laboratory, Teddington, for the gift of several pounds of 60 to 70 per cent 1-methylnaphthalene.

At the suggestion of Dr J. L. Simonsen the process was elaborated by preparation of the *p*-toluidine salt of the sulphonic acid. This salt could readily be crystallized from water and it had a sharp melting point: the recovered 1-methylnaphthalene froze almost completely at −31°.

As an alternative route to 1-methylnaphthalene that from naphthalene *via* 1-chloromethylnaphthalene [10] was investigated, but the elimination of impurity (probably the 2-isomeride) from the 1-chloromethyl-compound proved difficult. Introduction of methyl by the Wurtz–Fittig or the Friedel–Crafts method gives poor results in the naphthalene series; methylation of naphthylmagnesium bromide (derived from the pure 1-bromonaphthalene) has yet to be investigated.

Experimental.

1-Methylnaphthalene. (i) *By reduction of* 1-*chloromethylnaphthalene*.[10] Crude 1-chloromethylnaphthalene obtained by the method of Grummitt and Buck [11] was distilled in small portions *in vacuo* and then crystallized from alcohol: it melted at 30° to 31° (Anderson and Short [12] give m. pt. 32°). The substance (and especially the vapour of its alcoholic solution) has a vesicant action on the hands and face.

To 26 g of the chloro-compound in 100 cc of ethyl alcohol was added a solution of sodium ethoxide (from 6 g of sodium and 40 cc of alcohol). On shaking with hydrogen at room temperature and 4 atm pressure in the presence of 4 g of a catalyst (palladium on strontium carbonate,[1, p. 508]) reduction proceeded rapidly. The filtrate from the reaction product was diluted with water and the hydrocarbon collected with the aid of ether. Finally, 17 g of liquid b. pt. 155° to 157°/60 mm was obtained. From its m. pt. (−39°) this specimen appeared to contain approximately 88 per cent of 1-methylnaphthalene. (1-Ethoxymethyl naphthalene is a possible impurity.) The picrate melted at 138° to 139° instead of 141·5°.

(ii) *From tar-oil* via *the sulphonic acids*. The tar-oil supplied by the Chemical Research Laboratory, Teddington, had been washed with 60 per cent sulphuric acid, dried, and distilled; it melted at −14° (approximately 60 per cent 1-methylnaphthalene). 125 g of this oil were placed in a flask immersed in ice-water and stirred vigorously while 265 g of 98 per cent

sulphuric acid were run in *during* 15 *minutes*. The temperature was allowed to rise gradually from 5° to 25° at the finish, and the mixture then stood for 30 minutes. Water (320 cc) was stirred in, the temperature rising to 45°, and the mixture was left overnight at room temperature (usually without seeding). The crystalline sulphonic acid was collected on a sintered-glass funnel and pressed (86 g of moist solid). [The filtrate was extracted with pentane to remove any unsulphonated oil; it was then boiled while water was added to keep the b. pt. at 123°. From the distillate 20 g of oil m. pt. −19° or 68 per cent 1-methylnaphthalene were obtained.]

The crude, solid sulphonic acid was dissolved in water (250 cc) and the solution stirred at 80° with charcoal for 20 minutes, filtered, and allowed to cool. Concentrated sulphuric acid (60 cc) was stirred in and the solution allowed to stand several hours. It yielded 77 g of moist sulphonic acid which were dissolved in 125 cc of warm water. Concentrated hydrochloric acid (200 cc) was added at 70°, and on standing the mixture deposited light-coloured crystals of sulphonic acid. This when dried *in vacuo* over sodium hydroxide weighed 22 g. For further purification the *p*-toluidine salt was found satisfactory.[13, 14]

p-Toluidine Salt. 22 g. (0·1 mole) of the dry 1-methylnaphthalene-4-sulphonic acid were dissolved in water and neutralized with 2*N*-sodium hydroxide solution. While the solution was boiled, a hot solution of 11 g (0·1 mole) of *p*-toluidine in 12 cc of concentrated hydrochloric acid and 60 cc of water was added, together with a little charcoal. After filtration through glass-wool the liquid was allowed to cool: it deposited long needles (30 g) of the *p*-toluidine salt m. pt. 230° to 231·5°. Crystallization of these from 1 l of water containing 10 cc of acetic acid [13] gave 23 g of m. pt. 235°; recrystallization from 1 per cent acetic acid gave 18 g of m. pt. 236° to 237°, unchanged by further crystallization. (Found: C, 65·7; H, 5·9 per cent; $C_{18}H_{19}O_3SN$ requires C, 65·7; H, 5·8 per cent.) Prolonged boiling of the solutions causes decomposition of the toluidine salts.

1-Methylnaphthalene. The *p*-toluidine salt of 1-methylnaphthalene-4-sulphonic acid (15·5 g, m. pt. 236° to 237°), sodium hydroxide (3 g), and water (60 cc) were mixed in a distilling flask and distilled to dryness; water was added to the residue and the distillation repeated: the distillate became clear, and the smell of *p*-toluidine vanished. To the residue (sodium salt of the sulphonic acid) a mixture of water (50 cc) and sulphuric acid (50 g) was added. On distillation, an oil passed over with the steam and, when the volume in the distilling flask had fallen to half, water was dropped in. All the oil had been obtained when 350 cc of distillate had passed. The distillate was extracted with pentane (30 cc), the extract washed with sodium bicarbonate solution, dried with sodium sulphate, and distilled. 7 g (90 per cent yield) of hydrocarbon, b. pt. 244·5° ± 1°/760 mm, m. pt. −31° to −30°, were obtained. (Omission of the purification through the *p*-toluidine salt gave a less pure final product.) The best specimen had n_D^{20} 1·6174(5); n_D^{25} 1·6149(5); n_D^{40} 1·6070. Mair and Streiff [7] give m. pt. (extrapolated) −30·77° ± 0·06°; n_D^{20} (extrapolated) 1·6175; n_D^{25} 1·61494.

The picrate crystallized from ethyl alcohol in yellow-orange prisms m. pt. 141·5°; the *styphnate* formed yellow needles (from ethyl alcohol) m. pt. 135°. (Found: 10·7 per cent $C_{11}H_{10}{\cdot}C_6H_3O_8N_3$ requires N, 10·8 per cent) and the 1 : 3 : 5-trinitrobenzene complex (yellow needles from

alcohol) melted at 153·5° to 154·5°. (Found: N, 11·7 per cent. Calculated for $C_{11}H_{10}{\cdot}C_6H_3O_6N_3$, N, 11·8 per cent.) Triandaf,[15] who reported that the trinitrobenzene complex melted at 147° gave no data on the purity of the methylnaphthalene used.

2-Methylnaphthalene.

The purification of this hydrocarbon boiling at 241° and melting at 34° to 35° is relatively simple. Close fractional distillation of the coal-tar product eliminates apparently all the impurities except 1-methylnaphthalene (b. pt. 245°). Diphenyl (b. pt. 255°) if still present could be removed by conversion of the methylnaphthalenes into picrates: diphenyl picrate is unstable. The contaminating 1-methylnaphthalene forms solid solutions with the 2-isomeride (for the binary system see Coulson [8]), but repeated crystallization from alcohol suffices to give 2-methylnaphthalene of f. pt. 34·2°.

2-Methylnaphthalene has been synthesized on several occasions, but usually little care has been taken over the purification of the intermediates.

Experimental.

Several pounds of 2-methylnaphthalene *ex* coal-tar were kindly supplied by Dr E. A. Coulson and the Director, Chemical Research Laboratory, Teddington. On distillation through a short column it gave a main fraction b. pt. 129° to 131°/30 mm, m. pt. 31·7°. Three crystallizations from alcohol yielded a specimen of m. pt. and f. pt. 34·2°, unchanged by further crystallization. The specimen boiled at 241°/760 mm and had n_D^{40} 1·6017, which corresponds to n_D^{20} 1·6121. Mair and Streiff [7] give m. pt. 34·4°; n_D^{40} 1·6019. In a capillary tube, by the usual procedure, the m. pt. 34·5° to 35° was recorded.

The deep yellow *styphnate* crystallized well in prisms (some very slender) from ethyl alcohol. It melted at 129° to 129·5°, perhaps with some decomposition to styphnic acid and the hydrocarbon. (Found: N, 10·5 per cent. $C_{11}H_{10}{\cdot}C_6H_3O_8N_3$ requires N, 10·8 per cent.) The yellow-orange picrate crystallized from alcohol in slender prisms, m. pt. 116° to 117°, and the yellow 1 : 3 : 5-trinitrobenzene complex in long prisms, m. pt. 123·5° to 124°. (Found: N, 12·1 per cent. Calc. for $C_{11}H_{10}{\cdot}C_6H_3O_6N_3$, N, 11·8 per cent.)

1-Ethylnaphthalene.

This hydrocarbon was first prepared by Fittig and Remsen [20] by the reaction between 1-bromonaphthalene, ethyl bromide, and sodium. Carnelutti [21] repeated this preparation and made the picrate. The hydrocarbon has been reported as occurring in the "Stuppfett" of the mercury deposits of Idria.[22] Several workers [23, 24, 25, 26] have made 1-ethylnaphthalene by reduction of 1-acetonaphthone. 1-Naphthylmagnesium bromide has been ethylated (*a*) with diethyl sulphate [27] and (*b*) with ethyl *p*-toluene sulphonate.[28] Gilman and Kirby [29] methylated 1-naphthylmethyl chloride; Goldberg and Müller [30] converted α-tetralone into 1-ethynyltetralol which was reduced to 1-vinyltetralol, and passage over alumina gave 1-ethylnaphthalene.

As 1-acetonaphthone can be satisfactorily prepared by the Friedel–Crafts reaction and can be obtained as a crystalline solid, it is obviously a suitable intermediate for the preparation of a liquid hydrocarbon. The Friedel–Crafts reaction between naphthalene and acetyl chloride has been much investigated.[31-42, 45]

It is agreed that when nitrobenzene is used as solvent for the Friedel–Crafts reaction the product is mainly (80 to 95 per cent) 2-acetonaphthone, whereas with carbon disulphide or alkyl chlorides as solvent, up to 60 per cent of the product may be 1-acetonaphthone. Recently it has been claimed [42] that if the complex of the acid and aluminium chloride is made in the *absence* of naphthalene, and then the reaction with naphthalene is carried out in ethylene dichloride, ethylene dibromide, or methylene dichloride, 1-acetonaphthone is formed almost exclusively. The action of ketene on naphthalene is said to yield 1-acetonaphthone.[43]

The picrate of 1-acetonaphthone (m. pt. 119°) is readily separated from the more soluble picrate of the 2-isomeride (m. pt. 85°) and on removal of the picric acid the ketone can be obtained in crystalline state, melting at 10° to 11°. Reduction by the Wolff–Kishner process is satisfactory.

Experimental.

1-*Acetonaphthone.* 156 g (2 moles) of freshly distilled acetyl chloride and 128 g (1 mole) of naphthalene were dissolved in 500 cc of carbon disulphide in a 2-l flask cooled in ice-water. 133 g (2 moles) of powdered aluminium chloride were added in small quantities whilst the solution was stirred mechanically at 0° for 1 hour. After having stood for 24 hours at room temperature this mixture yielded 60 g of unchanged naphthalene and 72 g of crude acetonaphthone mixture, b. pt. 145° to 160°. On redistillation, 45 g were obtained boiling at 125° to 128°/0·15 mm n_D^{10} 1·6338, n_D^{20} 1·6295. When the redistilled ketone was dissolved in alcohol containing 1 equivalent of picric acid the solution deposited picrate melting at 114° to 116°; recrystallization gave yellow needles, m. pt. 118° to 119° (unchanged by further crystallization). In the literature this picrate is given melting points varying from 116° to 120°.[44]

When the pure picrate (m. pt. 118° to 119°, 66 g) was decomposed with warm sodium carbonate solution in the presence of a layer of benzene it gave 25 g of 1-acetonaphthone, m. pt. 10·2°, n_D^{20} 1·6282. Lock [41] gives m. pt. 10·5°; Bramwyche [45] also prepared a specimen from 1-naphthonitrile and recorded m. pt. 10·3°. But as the m. pt. has also been recorded [26, 32] as 34° the substance may be dimorphous; on the other hand less care was taken with the preparations which gave the high-melting ketone.

Reduction of 1-*Acetonaphthone.* Although Clemmensen [24] claimed a small yield of hydrocarbon by reduction of 1-acetonaphthone with amalgamated zinc and hydrochloric acid, repetition of his procedure gave only a gummy product. The Wolff–Kishner process gave good yields, but the formation of the semicarbazone was slower than usual.

1-Acetonaphthone (8·5 g, 0·05 mole) in alcohol (20 cc) was added to a solution of semicarbazide hydrochloride (14 g, 0·12 mole) and sodium acetate trihydrate (16 g) in hot water (50 cc); the mixture was refluxed for half an hour. The semicarbazone which crystallized out during the boiling was collected, washed with water, once with cold alcohol, and dried: 10·5 g

(93 per cent yield) of m. pt. 222° to 224° were obtained, and further purification was unnecessary. When this semicarbazone (10·5 g) was heated for twenty hours in a sealed tube with sodium ethoxide solution (2·5 g of sodium and 25 cc of alcohol) it gave 6·4 g (90 per cent yield) of hydrocarbon boiling at 133° to 135°/18 mm. Other reductions gave 85 and 90 per cent yields respectively.

Purification. 15·2 g (1 mole) of crude 1-ethylnaphthalene, 22·7 g. (1 mole) of picric acid, and 160 cc of alcohol gave 27· 2g of yellow picrate, m. pt. 98·5° to 99° and a second crop (6 g) of m. pt. 98° to 98·5°. The latter was recrystallized until it melted at 98° to 99°. The 1-ethylnaphthalene recovered from the pure picrate distilled at 135° to 136°/18 mm; on redistillation it gave a small fraction, b. pt. 135° to 136°/18 mm, m. pt. −14° to −13·5°, n_D^{20} 1·6053, and a main fraction, b. pt. 136°/18 mm, 259°/760 mm; m. pt. −13·5° to −13°; n_D^{20} 1·6062.

The *styphnate* crystallized from ethyl alcohol in yellow (slightly orange) prisms melting at 111° to 113°, with some decomposition into styphnic acid. (Found: N, 10·7 per cent. $C_{12}H_{12}{\cdot}C_6H_3O_8N_3$ requires N, 10·5 per cent.)

Sulphur-yellow needles of the 1 : 3 : 5-*trinitrobenzene complex* crystallized from ethyl alcohol and melted at 111·5° to 112°. (Found: N, 11·2 per cent. $C_{12}H_{12}{\cdot}C_6H_3O_6N_3$ requires N, 11·4 per cent.)

2-Ethylnaphthalene.

Kruber and Schade [46] reported the isolation of 2-ethylnaphthalene from coal-tar. All the obvious methods have been used by various workers in the preparation of this hydrocarbon.[34, 40, 47–52]

2-Acetonaphthone can readily be prepared in quantity by acetylation of naphthalene in nitrobenzene solution. Acetylation of tetralin in carbon-disulphide solution, followed by dehydrogenation, is more troublesome. The ketone is a highly crystalline substance, reducible through its semicarbazone to the hydrocarbon.

Experimental.

2-Acetonaphthone. (i) *From tetralin*, following Barbot [52] and Hesse.[50] 75 g (0·56 mole) of powdered aluminium chloride covered with carbon disulphide (420 cc) were stirred and cooled (ice-water) while a solution of acetyl chloride (46 cc, 0·6 mole) in tetralin (67·5 cc, 0·5 mole) was slowly added. After 1½ hours at 0° to 5° and then 1½ hours at room temperature the mixture was worked up to yield a main fraction (79 g, 91 per cent) b. pt. 158° to 160°/16 mm. Redistillation gave a fraction of b. pt. 155°/12 mm and m. pt. −13° to −11°. Barbot recorded b. pt. 161°/16 mm.

Dehydrogenation of this tetrahydroacetonaphthone with sulphur (Barbot [52]) gave a viscous liquid (b. pt. 140° to 155°; 70 per cent yield) which solidified. On crystallization from alcohol or from ligroin the pure ketone of constant m. pt. 53° to 54° was obtained.

(ii) *From naphthalene.* The addition of aluminium chloride to a nitrobenzene solution of naphthalene and acetyl chloride at −3° to −5° gave a smooth reaction until the last of the aluminium chloride was added. A sudden evolution of hydrogen chloride then occurred, the mixture darkened and the temperature rose rapidly to +5°. (Compare Lévy.[40]) The main

fraction of the product (obtained in 56 per cent yield) melted at 45°; it was recrystallized to m. pt. 53° to 54°.

2-Ethylnaphthalene. As the Clemmensen method of reduction gave a tar, the ketone was converted into the semicarbazone (obtained readily in good yield, melting at 225° to 227°, crude. Lock [41] gives m. pt. 234° to 235° for the pure substance.) On heating in 9-g batches with sodium ethoxide solution (2·5 g. of sodium and 25 cc of alcohol) for 20 hours at 190° the semicarbazone gave 80 per cent yields of crude 2-ethylnaphthalene, b. pt. 136° to 138°/20 mm. Conversion to the yellow-orange picrate m. pt. 77° to 77·5°, and then removal of the picric acid gave pure 2-ethylnaphthalene, b. pt. 131° to 132°/18 mm, 258°/760 mm, m. pt. −7°, n_D^{20} 1·5999.

The *styphnate* could not be prepared in ethyl alcoholic solution, but when made in *iso*propyl alcohol it formed sulphur-yellow prisms; these melted at 88° to 90°, decomposing to styphnic acid and the hydrocarbon. (Found: N, 10·5 per cent. $C_{12}H_{12}{\cdot}C_6H_3O_8N_3$ requires N, 10·5 per cent.) Sulphur-yellow needles of the 1 : 3 : 5-*trinitrobenzene complex* were prepared in ethyl alcoholic solution; as they smelt slightly of the hydrocarbon they were recrystallized from *iso*propyl alcohol and then melted at 87° to 88°. (Found: N, 11·6 per cent. $C_{12}H_{12}{\cdot}C_6H_3O_6N_3$ requires N, 11·4 per cent.)

1-*n*-Propylnaphthalene.

Two preparations of 1-*n*-propylnaphthalene are recorded in the literature [2, 3]; only one solid derivative of this (liquid) hydrocarbon has been described, namely the picrate for which Bargellini and Melacini [2] give m. pt. 141° to 142°, while Roblin, Davidson, and Bogert [3] record 92°. The American authors suggest that Bargellini and Melacini have confused their specimens of 1- and 2-*n*-propylnaphthalene, but this suggestion does not explain the discrepancy. (The picrate of 1-methylnaphthalene melts at 141° to 142°.)

Following the method of Rousset [33] the Italian workers prepared a mixture of 1- and 2-naphthylethyl ketones from which they separated the sparingly soluble picrate of the 1-isomeride. On regenerating the ketone and then reducing it by a lengthy treatment (boiling for 7 to 8 days) with hydriodic acid they obtained a hydrocarbon of b. pt. 274° to 275°, yielding a picrate melting at 141° to 142°. Bogert and his co-workers [3] in cyclizing 1-phenyl-6-hydroxyheptane with 90 per cent sulphuric acid isolated a substance which, on dehydrogenation, gave a naphthalene boiling at 275° to 276° and yielding a picrate of m. pt. 91° to 92°. They then repeated the preparation *via* the ketone (following Bargellini), but reduced by the Clemmensen method and obtained a hydrocarbon which yielded a picrate melting at 92°.

In this investigation 1-*n*-propylnaphthalene was prepared first *via* the ketone and secondly from pure 1-bromonaphthalene *via* 1-allylnaphthalene. The two specimens had the same boiling point, melting point, and refractive index. Several preparations of the picrates were made: the first preparation melted at 72° to 73°, but in all other cases the picrate melted between 84° and 88°.

As there were indications of the instability of the picrate the binary

system, picric acid–1-*n*-propylnaphthalene was investigated : the system showed formation of a 1 : 1 complex with a non-congruent m. pt. at 85° to 86°. Instability of the molecular compound in alcoholic solution was therefore to be expected.

The styphnate was too unstable to be isolated, but the 1 : 3 : 5-*trinitrobenzene complex* was a sharp-melting substance suitable for the identification of the hydrocarbon.

The refractive index of allyl bromide appears to need revision.

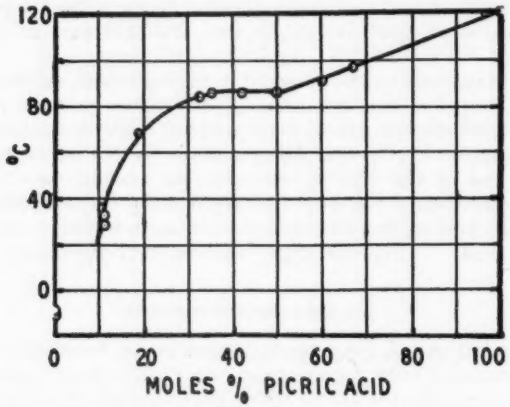

FIG. 1.

1-*n*-PROPYLNAPHTHALENE-PICRIC ACID.

Experimental.

1-*Naphthylethyl Ketone.* Pure propionic acid (215 g, b. pt. 140° to 141°) was converted into the chloride in a reflux apparatus into which phosphorus trichloride (250 g) was slowly dropped from a tap funnel. The mixture was heated until the evolution of hydrogen chloride had slackened (1 hour) and was then distilled (b. pt. 80° to 84° ; yield 227 g). Further purification was effected by heating the chloride under reflux for 3 hours with 3 to 4 g of anhydrous sodium propionate [55] and then fractionating with a glass Dufton column. The specimen boiled at 80° to 82°.

Naphthalene (160 g, 1·25 moles) was dissolved in carbon disulphide (500 cc) in a 3-l, three-necked flask fitted with a mechanical stirrer and a tap funnel. Powdered aluminium chloride (375 g, 2·8 moles) was added and then, with stirring, propionyl chloride (92·5 g, 1 mole) was slowly dropped in. There was a steady evolution of hydrogen chloride and the carbon disulphide was allowed to boil gently ; later the flask was heated on the water-bath. (This heating and the large excess of aluminium chloride probably account for the low yield obtained.) On working up in the usual way the carbon disulphide solution gave 41 g (22 per cent yield) of a colourless mixture of ketones b. pt. 150° to 151°/3 mm (main fraction).

The mixture of ketones (20·4 g) was added to a hot solution of picric acid (24·8 g, 1 equiv) in alcohol ; on cooling, a yellow picrate (36 g) was obtained.

Recrystallization from alcohol gave 31 g of picrate melting sharply at 80°, unchanged by further crystallization. Rousset [33] gives 77° to 78° as the melting point of the picrate of 1-naphthylethyl ketone.

On decomposition with warm sodium carbonate solution in the presence of a layer of pure benzene, this picrate (31 g) gave 11·2 g. (81 per cent yield) of colourless oil, b. pt. 157°/5 mm, n_D^{20} 1·6122. Rousset [33] gives b. pt. 166° to 168°/8 mm.

Oxidation: The ketone (4 g), dioxane (30 cc), and dry selenium dioxide (2 g) were heated for two hours; a further 2 g of selenium dioxide was added and the mixture heated for 3 hours. After standing overnight the liquid was decanted from the selenium; on addition of water a red oil (presumably mainly the diketone) was precipitated. This oil was isolated (with the aid of ether) and then added slowly to 30 per cent hydrogen peroxide solution (20 cc) with simultaneous addition of 20 cc of 10 per cent sodium hydroxide solution: the mixture was allowed to stand half an hour.

After removal of any unchanged ketone by extraction with ligroin the alkaline liquid was acidified, giving 1·3 g of solid. This acid, crystallized from toluene–ligroin mixture, melted at 161°. (α-Naphthoic acid melts at 161°.)

Reduction of 1-Naphthylethyl Ketone. The ketone (11 g, 0·075 mole) in alcohol (50 cc) was added to a solution of semicarbazide (15·5 g, 0·14 mole) and sodium acetate trihydrate (20 g) in warm water (50 cc). While the mixture was heated under reflux a further 50 cc of alcohol was added to obtain a homogeneous solution. After 30 minutes' boiling, the solution, on cooling, deposited crystals of the semicarbazone; addition of water gave another crop. (Total yield, 12·8 g, 88 per cent.) A small portion of *semicarbazone*, twice crystallized from alcohol; melted at 182° to 183°. (Found: N, 17·4 per cent. $C_{14}H_{15}ON_3$ requires N, 17·4 per cent.)

Heating the crude semicarbazone (12 g) with a solution of sodium ethoxide (5 g of sodium in 50 cc of alcohol) at 200° for 24 hours gave the hydrocarbon which isolated with the aid of pentane, distilled at 124°/8 mm (6·2 g, 73 per cent yield). Redistillation gave a main fraction b. pt. 272° to 273°/760 mm, m. pt. −13° to −12°, n_D^{20} 1·5922. (Found: C, 91·7; H, 8·5 per cent. Calc., C, 91·7; H, 8·2 per cent.)

Molecular Compounds. On cooling a hot solution of equivalent amounts of the hydrocarbon and of styphnic acid in alcohol or in glacial acetic acid only styphnic acid separated out.

From a solution of the hydrocarbon (0·82 g) and picric acid (1·12 g) in ethyl alcohol (17 cc of 95 per cent) deep yellow needles of a picrate, m. pt. 72° to 74° separated. (Found: C, 56·8; H, 4·2; N, 10·7 per cent. Calc. for $C_{13}H_{14}{\cdot}C_6H_3O_7N_3$, C, 57·1; H, 4·3; N, 10·5 per cent.) These needles in polarized light had straight extinction. On keeping for some weeks they changed partly and the m. pt. spread over the range 73° to 88°. Later preparations of the picrate, although made in the same way as described above, all melted between 84° and 87°, but left some solid (? picric acid) in the capillary tube up to 91°. These crystals were rectangular prisms, opaque between crossed nicols. (Found, in picrate of m. pt. 84° to 87°, N, 10·8 per cent. Calc., N, 10·5 per cent.) On mixing the two specimens of picrate (72° and 84°) a mixture of m. pt. 73° to 85° was obtained. This

appears to be a case of dimorphism, but with only a slow change from the lower- to the higher-melting form.

The 1 : 3 : 5-*trinitrobenzene complex*, crystallized from alcohol, melted at 86° to 87°. (Found : N, 10·6 per cent. $C_{13}H_{14}{\cdot}C_6H_3O_6N_3$ requires N, 10·9 per cent.)

1-n-*Propylnaphthalene* via 1-*bromo-* and 1-*allylnaphthalene*. 1-Bromonaphthalene was purified by the process of Jones and Lapworth.[56] Three crystallizations from absolute alcohol gave a product of m. pt. 6·1°. (Jones and Lapworth give 6·2°. The metastable form, m. pt. 1° to 2°, changes on rubbing with the thermometer to the stable form, m. pt. 6·2°.)

The Grignard reagent, prepared from pure 1-bromonaphthalene (41·4 g, 0·2 mole), magnesium turnings (7·2 g, 0·3 mole), and 100 cc of dry ether, set solid, but was dissolved [57] by addition of dry benzene (50 cc). Excess of magnesium was removed by filtration through a plug of cotton wool, the turnings being washed with 50 cc of dry benzene.

Allyl bromide was washed with ferrous sulphate solution until it failed to give the ferric thiocyanate test for peroxides, and it was then distilled through a glass Dufton column. It boiled at 70·0° to 70·4°/756 mm and on re-distillation a main fraction of b. pt. 70·2° to 70·4°/756 mm (70·4° to 70·6°/760 mm), n_D^{20} 1·4694, was obtained. Another batch of allyl bromide, from a different source, was washed with ferrous sulphate and then dried with phosphorus pentoxide. This specimen also gave a large main fraction of n_D^{20} 1·4694 : it seems that the value n_D^{20} 1·46545 generally quoted [58] is wrong.

The solution of the Grignard reagent was then added slowly to a stirred solution of allyl bromide (24·2 g) and the mixture refluxed gently for 10 hours. An 84 per cent yield (28 g) of the crude hydrocarbon was obtained, and on distillation the main fraction, b. pt. 140° to 142°/18 mm, had n_D^{25} 1·6098. The deep-yellow picrate, crystallized from methanol, melted at 74° to 75°. (Found : N, 10·6 per cent. Calc for $C_{13}H_{12}{\cdot}C_6H_3O_7N_3$, N, 10·5 per cent.) Fieser and Hershberg [57] gave for 1-allylnaphthalene b. pt. 127·5° to 128·5°/8 mm; n_D^{25} 1·6089; picrate, m. pt. 68° to 69°; N, 11·0 per cent.

Reduction. 18 g of the olefin in 40 cc of dry ethanol were shaken with Raney nickel (2 g) and hydrogen at 2 atm. Within 10 minutes the theoretical volume of hydrogen was absorbed and the mixture was shaken for 30 minutes longer. The resulting 1-*n*-propylnaphthalene (82 per cent yield) boiled at 271° to 272°/758 mm, and had, n_D^{20} 1·5923. On cooling strongly it crystallized, and when the tube was placed in a mass of cotton wool, the thermometer became steady at −13° to −12°. When the crystals were rubbed, however, the temperature rose and there was a second m. pt. at −9°. The picrate melted unsharply at 84° to 88° and the trinitrobenzene complex melted at 86° to 87°.

Binary System, Picric Acid–1-*n*-Propylnaphthalene.

Mixtures, total weight 3 to 4 g, of picric acid and the pure hydrocarbon were made up, carefully melted, stirred with an Anschütz thermometer, and cooled. When a moderate amount of solid had formed the tube was placed in the air-jacket of a Beckmann-type melting-point apparatus. The temperature of the well-stirred bath was kept 2° to 3° higher than that

of the melting picrate; the melt was stirred with the thermometer and the temperature at which the fine needles of the complex finally disappeared was taken as the m. pt. of the mixture. This procedure was more satisfactory than taking the freezing points. Except for mixtures with a low content (5 to 15 per cent) of picric acid the m. pt. were sharp and reproducible within 1°.

TABLE II.

Mols. of picric acid, per cent.	Mols. of H.C., per cent.	M. pt., ° C.
0	100	−9 and −13
10·6	89·4	30 to 35
19·0	81·0	68
32·4	67·6	84
35·5	64·5	86
42·0	58·0	85 to 86
50·0	50·0	84 to 86
60·0	40·0	91 to 92
67·0	33·0	97
100.	0	121

2-*n*-PROPYLNAPHTHALENE.

L. Roux,[34] who prepared a hydrocarbon by the Friedel–Crafts reaction between naphthalene and *n*-propyl bromide, considered, in view of the known tendency of *n*-alkyl halides to rearrange in the presence of aluminium chloride, that his product was 2-*iso*propylnaphthalene. (It boiled at 265° and yielded a picrate melting at 89° to 90°). The alkylnaphthalene obtained by Bargellini and Melacini[2] by reduction of 2-naphthylethyl ketone boiled at 277° to 279° and gave a picrate melting at 90° to 92°.

As 2-naphthylethyl ketone is an easily purified crystalline solid it is a suitable intermediate for the preparation of the hydrocarbon. It could, moreover, be reduced in reasonable yield by the Clemmensen method, whereas the corresponding naphthylmethyl ketone gave a poor result. The separation from 1-naphthylethyl ketone by means of the picrates[2] was unsatisfactory, but use of nitrobenzene instead of carbon disulphide in the Friedel–Crafts reaction gave good yields of 2-naphthylethyl ketone.[59] The pure ketone on reduction gave 2-*n*-propylnaphthalene which formed a picrate melting at 90°. This agrees with Bargellini and Melacini's figure[2] and there is no support for Bogert's[3] suggestion of interchanging the figures for the melting points of 1- and of 2-*n*-propylnaphthalene.

2-Naphthylethyl Ketone. (Following the procedure of Lévy[40] for 2-naphthylmethyl ketone.) Naphthalene (128 g, 1 mole) was dissolved in nitrobenzene (540 cc) which had been distilled with steam and dried with calcium chloride; propionyl chloride (101 g, 1·1 mole) was added. The solution was stirred mechanically in a 1500-cc flask cooled in a mixture of ice and salt while finely powdered, anhydrous aluminium chloride (102 g, 1·1 mole) was added in 10-g portions during two hours, the temperature being kept at −5° to −3°. The mixture was left at room temperature for 6 hours, and the olive-green solution was then poured into dilute hydrochloric acid and ice. From the washed and dried nitrobenzene layer

the ketone, b. pt. 156° to 160°/5 mm was obtained in 57 per cent yield (96·3 g). Two crystallizations from alcohol gave 56 g of colourless ketone m. pt. 57° to 58°, and a third crystallization raised it to 59°, but no further increase could be obtained. Buu-Hoï and Cagniant [59] claim m. pt. 60°. That the ketone was a β-substituted naphthalene was proved by oxidation with selenium dioxide and then with hydrogen peroxide as for the 1-naphthylethyl ketone (p. 687). The crude oxidation product melted at 182° to 183° and crystallization from toluene–ligroin mixture gave an acid of m. pt. 183° to 184°. β-Naphthoic acid melts at 185°.

2-n-*Propylnaphthalene*. Reduction of 2-naphthylethyl ketone: (*a*) by the Clemmensen method.—The ketone (15·6 g) in alcohol (50 cc) was added to amalgamated zinc (40 g) and conc hydrochloric acid (40 cc). While the mixture was heated for ten hours, conc hydrochloric acid (5 portions, each of 10 cc) was added. The product, isolated with the aid of pentane, gave 6·5 g (46 per cent yield) of hydrocarbon, b. pt. 126° to 130°/7 mm, leaving 4·8 g of resinous material.

(*b*) By the Wolff–Kishner method.—The ketone (20·9 g) gave 26·9 g (98 per cent yield) of crude semicarbazone, which was not purified. This semicarbazone in three portions was heated at 200° for 24 hours with, in each tube, a solution of sodium ethoxide (2·5 g of sodium in 25 cc of alcohol). A pentane extract of the combined products was washed with dilute acid, dried, and distilled, giving 9·2 g (49 per cent yield, but some was lost) of crude hydrocarbon. Re-distillation gave 8·2 g of colourless oil b. pt. 133° to 134°/14 mm, n_D^{20} 1·5875. Repeated distillation gave a final product of b. pt. 273° to 274°/760 mm; m. pt. −3°; n_D^{20} 1·5872. (Found: C, 91·7; H, 8·2 per cent. Calc. C, 91·8; H, 8·2 per cent.)

When a hot acetic-acid solution of the hydrocarbon was mixed with one of styphnic acid an orange colour developed, but on cooling only styphnic acid, m. pt. 175°, separated; the addition complex was unstable.

The deep-yellow picrate (from ethyl alcohol) melted at 90°. (Found: N, 10·5 per cent. Calc. for $C_{13}H_{14}{\cdot}C_6H_3O_7N_3$, N, 10·5 per cent.) Bargellini and Melacini [2] give m. pt. 90° to 92°.

The 1 : 3 : 5-*trinitrobenzene complex*, long needles from alcohol, melted at 99°. (Found: N, 10·7 per cent. $C_{13}H_{14}{\cdot}C_6H_3O_6N_3$ requires N, 10·9 per cent.)

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THE PREDICTION OF VAPOUR–LIQUID EQUILIBRIA FOR TERNARY MIXTURES FROM THE DATA OF BINARY SYSTEMS.

By Yu-Ming Li* and James Coull.*

Synopsis.

In this paper an approximate derivation of equations in vapour–liquid equilibrium relationships has been made. Although the resulting equations are similar to those previously published, it is believed that they are in a more reasonable form from a theoretical point of view. The range of their validity is implied by the assumptions from which they are derived. Work is confined to binary and ternary systems; the same method can, however, be extended to quaternary systems or even more complex mixtures. The equations are tested with published experimental data, and the calculated results show good agreement with the observed values.

Recently a considerable number of papers [1,4,14,15] covering the methods of correlating vapour–liquid equilibrium data for complex non-ideal solutions have been published. In this paper the van Laar type of equation for predicting vapour–liquid equilibria is studied. An approximate derivation of the equations is presented, and the range of their validity is determined.

Internal Energy Change in Mixing.

It is at present beyond the power of existing laws and theories to deduce accurately the internal properties of liquids. No effort has been made in this paper to present a thorough study in this field. As a method of approach only some qualitative deductions (or, strictly speaking, some assumptions) have been made and treated below.

Consider that two liquids 1 and 2 are brought together under constant pressure. The addition of one kind of molecules to the other will reduce the number of collisions between molecules of the same kind. And, at the same time, collisions between molecules 1 and 2 arise. The internal energy will be changed as collisions between different kinds of molecules occur. In cases where no chemical effects take place, the net change of internal energy due to mixing is now roughly expressed as

$$\begin{aligned}\Delta E_{12} &= 2ZE_{12} - (ZE_{11} + ZE_{22}) \\ &= Z(2E_{12} - E_{11} - E_{22}) \quad . \quad . \quad . \quad . \quad . \quad (1)\end{aligned}$$

where $2Z$ is the collision frequency between molecules 1 and 2, and E_{11}, E_{22}, and E_{12} are the resulting energies due to collisions between molecules 1 and 1, 2 and 2, and 1 and 2 respectively. In the case of an ideal solution, $E_{11} = E_{22} = E_{12}$, or $2E_{12} - E_{11} - E_{22} = 0$.

Since E_{11}, E_{22}, and E_{12} are constant at constant temperature, it follows that the change of internal energy on mixing is shown to be

$$\Delta E_{12} = CZ_{12} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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where $Z_{12} = 2Z$. The proportionality constant, C, which is dependent on the character of the molecules taking part in the collisions, is zero in the case of an ideal solution.

In the case of gases, there has been derived the following expression [7] for the total number of collisions, $\bar{z}_{AB}$, per unit volume per unit time between molecules A and B in a mixture of gases :—

$$\bar{z}_{AB} = 2c_A c_B d^2_{AB} \left\{\frac{2\pi(m_A + m_B)kT}{m_A m_B}\right\}^{1/2} \quad . \quad . \quad . \quad . \quad (3)$$

where c_A and c_B represent the number of molecules per unit volume of gases A and B respectively; d_{AB} is the distance between centres on collision, and m_A and m_B are the masses of the molecules.

Or, at constant temperature,

$$\bar{z}_{AB} = C' c_A c_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where C' is a constant at constant temperature.

It may also be expected that the same relation holds qualitatively for liquids. Then the collision frequency between liquid molecules 1 and 2 per unit volume is

$$\bar{z}_{12} = C'' \bar{n}_1 \bar{n}_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where C'' is a constant at constant temperature, and $\bar{n}_1$ and $\bar{n}_2$ are numbers of moles per unit volume of liquids 1 and 2 respectively.

Now, consider n_1 moles of liquid 1 having a molar volume V_1 and n_2 moles of liquid 2 having a molar volume V_2 are brought together, and assume no volume change takes place on mixing, then the energy change attending mixing is given by the relation :—

$$\begin{aligned}\Delta E_{12} &= CZ_{12} \\ &= C(n_1V_1 + n_2V_2)\bar{z}_{12} \\ &= C(n_1V_1 + n_2V_2)C'' \left(\frac{n_1}{n_1V_1 + n_2V_2}\right)\left(\frac{n_2}{n_1V_1 + n_2V_2}\right) \\ &= \frac{CC''n_1n_2}{n_1V_1 + n_2V_2}\end{aligned}$$

$$\text{Or,} \quad \Delta E_{12} = \frac{a_{12}n_1n_2}{n_1V_1 + n_2V_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where a_{12} is a constant at constant temperature.

Actually with non-ideal solutions this is not the case; for volume changes do occur on mixing. However, Equation (6) will still hold, if the partial molal volumes b_1 and b_2 of components 1 and 2 are used. When these partial molal quantities are introduced, Equation (6) becomes

$$\Delta E_{12} = \frac{a_{12}n_1n_2}{n_1b_1 + n_2b_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For a ternary mixture, one may consider the internal energy change on mixing as the result of three different kinds of collisions between different kinds of molecules (namely, 1 and 2, 1 and 3, and 2 and 3). And, by the

same reasoning, the internal energy change for a ternary mixture can be written

$$\Delta E_{123} = \frac{a_{12}n_1n_2 + a_{13}n_1n_3 + a_{23}n_2n_3}{b_1n_1 + b_2n_2 + b_3n_3} \quad . \quad . \quad . \quad . \quad (8)$$

Free Energy Change in Mixing.

When the internal energy change on mixing is known, it will not be difficult to formulate an expression relating it to the free energy change, if proper assumptions are made.

First, neglect the volume change on mixing, so that one may immediately write enthalpy change,

$$\Delta H = \Delta E$$

This will not introduce any appreciable error, as the $\Delta(PV)$ term is small in comparison with ΔE.

The second assumption due originally to Scatchard [13] is that, under the conditions stated by Hildebrand,[9, 10] "When orienting and chemical effects are absent and the distribution and orientation are random," the entropy change on mixing is the same as for an ideal solution. Or, the entropy change due to mixing n_1 moles of liquid 1 with n_2 moles of liquid 2 under such conditions is

$$\Delta S_{12} = -n_1R \ln x_2 - n_2R \ln x_2 \quad . \quad . \quad . \quad . \quad (9)$$

where x_1 and x_2 are the mol fractions.

Because of the well-known connexion between entropy and probability, this assumption seems reasonable wherever this randomness exists.

It follows, therefore, on mixing n_1 moles of liquid 1 with n_2 moles of liquid 2 the free energy change is

$$\begin{aligned} \Delta F_{12} &= \Delta H_{12} - T\Delta S_{12} \\ &= \Delta E_{12} + n_1RT \ln x_1 + n_2RT \ln x_2 \quad . \quad . \quad (10) \end{aligned}$$

Equation (10) can be written

$$F_{12} = n_1F_1^0 + n_2F_2^0 + n_1RT \ln x_1 + n_2RT \ln x_2 + \Delta E_{12} \quad . \quad (11)$$

where F_{12} is the free energy of the mixture, and F_1^0 and F_2^0, that of the pure components.

For the partial free energy of component 1, $\bar{F}_1$, it follows that

$$\bar{F}_1 = \frac{\delta F_{12}}{\delta n_1} = F_1^0 + RT \ln x_1 + \frac{\delta}{\delta n_1}(\Delta E_{12}) \quad . \quad . \quad (12)$$

Equation (12) can be written

$$\begin{aligned} \bar{F}_1 - F_1^0 &= RT \ln a_1 \\ &= RT \ln x_1 + \frac{\delta}{\delta n_1}(\Delta E_{12}) \quad . \quad . \quad . \quad (13) \end{aligned}$$

where a_1 is the activity of component 1.

Or,

$$RT \ln \gamma_1 = \frac{\delta}{\delta n_1}(\Delta E_{12}) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where γ_1 is the activity coefficient of component 1.

The same relation can be obtained for a component i in a mixture of r components, if the same conditions prevail.

Or,
$$RT \ln \gamma_i = \frac{\delta}{\delta n_i}(\Delta E_{1\ldots r}) \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where γ_i is the activity coefficient of component i, and $\Delta E_{1\ldots r}$ is the internal energy change attending the formation of the mixture.

Activity Coefficients as Functions of Mol Fractions.

1. *Binary Systems.*

Substitution of Equation (7) in Equation (14) gives

$$RT \ln \gamma_1 = \frac{\delta}{\delta n_1}\left(\frac{a_{12} n_1 n_2}{b_1 n_1 + b_2 n_2}\right) \quad . \quad . \quad . \quad . \quad (16)$$

Let
$$k_{12} = \frac{a_{12}}{2 \cdot 3R},$$

and neglect the effect of composition on the partial molal volume (*i.e.*, assume that b is nearly independent of the composition *), one obtains

$$\begin{aligned} T \log \gamma_1 &= \frac{\delta}{\delta n_1}\left(\frac{k_{12} n_1 n_2}{b_1 n_1 + b_2 n_2}\right) \\ &= \frac{k_{12}/b_2 n_2^2}{(b_1 n_1 + b_2 n_2)^2} \\ &= \frac{k_{12}/b_2}{\left\{\left(\frac{b_1}{b_2}\right)\left(\frac{n_1}{n_2}\right) + 1\right\}^2} \\ &= \frac{1}{\left\{\left(\frac{b_1}{b_2}\right)\left(\frac{b_2}{k_{12}}\right)^{1/2}\left(\frac{x_1}{x_2}\right) + \left(\frac{b_2}{k_{12}}\right)^{1/2}\right\}^2} \end{aligned}$$

Or,
$$(T \log \gamma_1)^{-1/2} = \left(\frac{b_1}{b_2}\right)\left(\frac{b_2}{k_{12}}\right)^{1/2}\left(\frac{x_1}{x_2}\right) + \left(\frac{b_2}{k_{12}}\right)^{1/2} \quad . \quad . \quad . \quad (17)$$

Similarly,
$$(T \log \gamma_2)^{-1/2} = \left(\frac{b_2}{b_1}\right)\left(\frac{b_1}{k_{12}}\right)^{1/2}\left(\frac{x_2}{x_1}\right) + \left(\frac{b_1}{k_{12}}\right)^{1/2} \quad . \quad . \quad . \quad (18)$$

Thus, a plot of $(T \log \gamma_1)^{-1/2}$ versus x_1/x_2 should give a straight line having a slope $\left(\frac{b_1}{b_2}\right)\left(\frac{b_2}{k_{12}}\right)^{1/2}$ and an intercept $\left(\frac{b_2}{k_{12}}\right)^{1/2}$. Similarly, a plot of $(T \log \gamma_2)^{-1/2}$ versus x_2/x_1 should have a slope $\left(\frac{b_2}{b_1}\right)\left(\frac{b_1}{k_{12}}\right)^{1/2}$ and an intercept $\left(\frac{b_1}{k_{12}}\right)^{1/2}$. Once the intercepts are found, the constants $\left(\frac{b_1}{k_{12}}\right)^{1/2}$ and $\left(\frac{b_2}{k_{12}}\right)^{1/2}$ will be determined. And the ratio b_1/b_2 will be evaluated from the relation

$$\frac{b_1}{b_2} = \left\{\frac{(b_1/k_{12})^{1/2}}{(b_2/k_{12})^{1/2}}\right\}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

* A further discussion on b will be given later.

All these constants are subsequently used in ternary relations to predict ternary vapour–liquid equilibria.

Equations (17) and (18) are similar to the two suffix van Laar Equations which are presented in White's paper [14] as Equations (7) and (8), and in Wohl's paper [15] as Equations (11*a*) and (11*b*), but they are different both in form and in constants.

The constant k_{12} in Equations (17) and (18) is of the same power as that of $T \log \gamma$, while the equivalent constant in White's Equations (5) to (8) [14] is not so defined. Since b, representing the volume, should always be positive, a negative deviation from Raoult's law (*i.e.*, $T \log \gamma$ is negative) will result in an imaginary number for the constant where White's Equations (5) to (8) are used. This trouble is avoided in Equations (17) and (18) in the present paper, as it can be explained that when negative deviations appear, the proportionality constant a_{12} (which is equal to $2{\cdot}3Rk_{12}$) also becomes negative (*i.e.*, decrease of internal energy in mixing).

Most organic solutions follow Equations (17) and (18) closely through a considerable range of x-ratio (x_1/x_2). Agreement is especially good when the x-ratio is below 1. When the x-ratios become greater, most plots of $(T \log \gamma)^{-1/2}$ versus x-ratio are found to become erratic. It has been explained by White [14] that as the composition of the mixture approaches that of a pure component, the activity coefficient, γ, is nearly equal to 1 and therefore $(T \log \gamma)^{-1/2}$ approaches infinity, thus becoming more and more sensitive to experimental and computational errors or inconsistencies.

Equations (17) and (18) cannot be used when the vapour deviates appreciably from the ideal, as in the case of the system acetic acid–water where the acid molecules are associated.

When the effect of temperature on the k-constant is negligible, they can be applied to isobaric processes.

2. *Ternary Systems.*

Substitution of Equation (8) in Equation (15) gives

$$RT \ln \gamma_1 = \frac{\delta}{\delta n_1}\left(\frac{a_{12}n_1n_2 + a_{13}n_1n_3 + a_{23}n_2n_3}{b_1n_1 + b_2n_2 + b_3n_3}\right) \quad . \quad . \quad (20)$$

Let

$$k_{12} = a_{12}/2{\cdot}3R$$
$$k_{13} = a_{13}/2{\cdot}3R$$
$$k_{23} = a_{23}/2{\cdot}3R,$$

and neglecting the effect of composition on partial molal volume, one obtains :—

$$RT \log \gamma_1 = \frac{\delta}{\delta n_1}\left(\frac{k_{12}n_1n_2 + k_{13}n_1n_3 + k_{23}n_2n_3}{b_1n_1 + b_2n_2 + b_3n_3}\right)$$
$$= \frac{k_{12}b_2n_2 + k_{13}b_3n_3^2 + (k_{12}b_3 + k_{13}b_2 - k_{23}b_1)n_2n_3}{(b_1n_1 + b_2n_2 + b_3n_3)^2}$$
$$= \left\{\left(\frac{k_{12}}{b_1}\right)\left(\frac{b_2}{b_1}\right)x_2^2 + \left(\frac{k_{13}}{b_1}\right)\left(\frac{b_3}{b_1}\right)x_3^2 + \left[\left(\frac{k_{12}}{b_1}\right)\left(\frac{b_3}{b_1}\right) + \left(\frac{k_{13}}{b_1}\right)\left(\frac{b_2}{b_1}\right) - \left(\frac{k_{23}}{b_1}\right)\right]x_2x_3\right\} \Big/ \left\{x_1 + \left(\frac{b_2}{b_1}\right)x_2 + \left(\frac{b_3}{b_1}\right)x_3\right\}^2 \quad (21)$$

$$T \log \gamma_2 = \left\{\left(\frac{k_{12}}{b_2}\right)\left(\frac{b_1}{b_2}\right) x_1^2 + \left(\frac{k_{23}}{b_2}\right)\left(\frac{b_3}{b_2}\right) x_3^2 + \left[\left(\frac{k_{12}}{b_2}\right)\left(\frac{b_3}{b_2}\right) + \left(\frac{k_{23}}{b_2}\right)\left(\frac{b_1}{b_2}\right) - \left(\frac{k_{13}}{b_2}\right)\right] x_1 x_3\right\} \Big/ \left\{x_2 + \left(\frac{b_1}{b_2}\right) x_1 + \left(\frac{b_3}{b_2}\right) x_3\right\}^2 \quad (22)$$

$$T \log \gamma_3 = \left\{\left(\frac{k_{13}}{b_3}\right)\left(\frac{b_1}{b_3}\right) x^2{}_1 + \left(\frac{k_{23}}{b_3}\right)\left(\frac{b_2}{b_3}\right) x_2^2 + \left[\left(\frac{k_{13}}{b_3}\right)\left(\frac{b_2}{b_3}\right) + \left(\frac{k_{23}}{b_3}\right)\left(\frac{b_1}{b_3}\right) - \left(\frac{k_{12}}{b_3}\right)\right] x_1 x_2\right\} \Big/ \left\{x_3 + \left(\frac{b_1}{b_3}\right) x_1 + \left(\frac{b_2}{b_3}\right) x_2\right\}^2 \quad (23)$$

Equations (21) to (23) are similar to Wohl's equations (49*a*) to (49*c*),[15] but they are different both in form and in constants.

It may be expected that k_{12} (also k_{13} and k_{23}) is nearly independent of the presence of molecules other than those taking part in binary collisions to which k_{12} pertains. In other words k_{12} in a ternary mixture is the same as in a binary mixture. It is clear that all constants in the ternary relations, *i.e.*, Equations (21) to (23), can also be found in the binary relations, *i.e.*, Equations (17) and (18), except the three constants k_{23}/b_1, k_{13}/b_2, and k_{12}/b_3. These three constants can, however, be evaluated from the following relations :—

$$\left(\frac{k_{12}}{b_3}\right) = \frac{(k_{12}/b_1)_{12}}{(b_3/b_1)_{13}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24a)$$

$$\left(\frac{k_{13}}{b_2}\right) = \frac{(k_{13}/b_1)_{13}}{(b_2/b_1)_{12}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24b)$$

$$\left(\frac{k_{23}}{b_1}\right) = \frac{(k_{23}/b_2)_{23}}{(b_1/b_2)_{12}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24c)$$

Since the b-ratios in the ternary equations are read from the three binary systems made up of the three components, therefore, for consistency, the three binary systems should be restricted to a quantitative relation, namely,

$$\left(\frac{b_1}{b_2}\right)_{12} = \frac{(b_1/b_3)_{13}}{(b_2/b_3)_{23}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Once the above relation holds, Equations (21) to (23) can be used to evaluate the activity coefficients of a ternary mixture from the data of the three binary pairs made up of two of the three components.

To predict the vapour–liquid equilibria of a ternary mixture in an isobaric process, the following relation is used :—

$$P = p_1^0 x_1 \gamma_1 + p_2^0 x_2 \gamma_2 + p_3^0 x_3 \gamma_3 \quad . \quad . \quad . \quad . \quad (26)$$

where p_1^0, p_2^0, and p_3^0 are the vapour pressures of pure liquids of components 1, 2, and 3 respectively.

Thus, for a given composition under a total pressure P, the boiling temperature T is determined from Equations (21), (22), (23), and (26) by trial and error, provided that the vapour-pressure data of each component and constants of the three binary systems are at hand.

Prediction of Ternary Activity Coefficients.

By using Equations (21) to (23), activity coefficients for the ternary systems *n*-heptane–toluene–methanol, ethanol–methanol–water and *iso*-octane–toluene–phenol are predicted from the experimental data of the following binary systems :—

n-heptane–toluene [2]	methanol–water [5]
n-heptane–methanol [1]	*iso*octane–toluene [6]
toluene–methanol [1]	*iso*octane–phenol [6]
ethanol–water [3]	toluene–phenol [6]

Plots of $(T \log \gamma)^{-1/2}$ versus x-ratio for the above systems are shown in Figs. 1 to 3. From these plots the binary constants are read and tabulated in Table I.

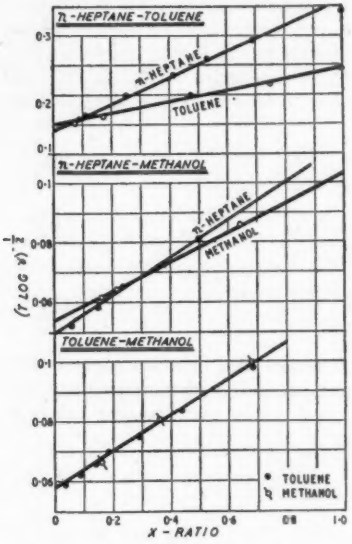

FIG. 1.

EVALUATION OF BINARY CONSTANTS.

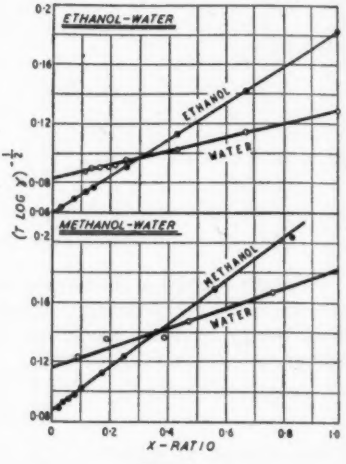

FIG. 2.

EVALUATION OF BINARY CONSTANTS.

For the system *iso*octane–phenol the published data are not reliable above 10 per cent of phenol.[6] Thus, on plotting $(T \log \gamma)^{-1/2}$ versus x-ratio, only one straight line belonging to phenol can be drawn, and consequently, only the constant $(b_{isooctane}/k_{isooctane\text{–}phenol})^{-1/2}$ can be read. To evaluate the constant $(b_{phenol}/k_{isooctane\text{–}phenol})^{-1/2}$, an assumption is made that the components in the ternary systems *iso*octane–toluene–phenol follow Equation (25) so closely that

$$\frac{b_{isooctane}}{b_{phenol}} = \left(\frac{b_{isooctane}}{b_{toluene}}\right)\left(\frac{b_{toluene}}{b_{phenol}}\right)$$

Once the ratio ($b_{isooctane}/b_{phenol}$) is evaluated from the above relation, the constant ($b_{phenol}/k_{isooctane\text{-}phenol}$) can be readily computated by using Equation (19).

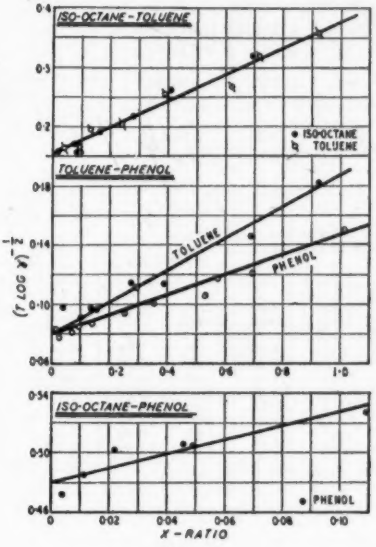

FIG. 3.

EVALUATION OF BINARY CONSTANTS.

TABLE I.

Binary Constants.

System.		Binary constants.*		
Component 1.	Component 2.	$\left(\frac{b_1}{k_{12}}\right)^{1/2}$.	$\left(\frac{b_2}{k_{12}}\right)^{1/2}$.	$\left(\frac{b_1}{b_2}\right)$.
n-Heptane	Toluene	0·15	0·14	1·15
n-Heptane	Methanol	0·0535	0·05	1·15
Toluene	Methanol	0·059	0·059	1·00
Ethanol	Methanol	($k_{12} = 0$)	($k_{12} = 0$)	(1·16)
Ethanol	Water	0·084	0·06	1·96
Methanol	Water	0·116	0·089	1·69
*Iso*octane	Toluene	0·155	0·155	1·00
*Iso*octane	Phenol	0·048	(0·048)	(1·00)
Toluene	Phenol	0·079	0·079	1·00

* Values in parenthesis are not read from Figs. 1 to 3.

The system ethanol–methanol obeys Raoult's law, and hence its *k*-constant is zero. To evaluate the *b*-ratio, the same assumption made for the system *iso*octane–phenol is used, so that

$$\frac{b_{ethanol}}{b_{methanol}} = \left(\frac{b_{ethanol}}{b_{water}}\right) \Big/ \left(\frac{b_{methanol}}{b_{water}}\right)$$

TABLE II.

Comparison of Experimental and Predicted Activity Coefficients.

System: *n*-Heptane–toluene–methanol.

$$T \log \gamma_1 = \frac{38{\cdot}6x_2^2 + 303x_3^2 + 91{\cdot}6x_2x_3}{(x_1 + 0{\cdot}87x_2 + 0{\cdot}87x_3)^2}$$

$$T \log \gamma_2 = \frac{58{\cdot}6x_1^2 + 287x_3^2 - 19x_1x_3}{(x_2 + 1{\cdot}15x_1 + x_3)^2}$$

$$T \log \gamma_3 = \frac{460x_1^2 + 287x_2^2 + 679x_1x_2}{(x_3 + 1{\cdot}15x_1 + x_2)^2}$$

1 refers to *n*-heptane.
2 refers to toluene.
3 refers to methanol.

Run No.	Temp., ° K.	Liquid composition (mol percentage).			Activity coefficients.					
					n-Heptane.		Toluene.		Methanol.	
		n-Heptane.	Toluene.	Methanol.	Predicted.	Expt.	Predicted.	Expt.	Predicted.	Expt.
1	333·87	6·84	8·30	84·86	7·50	7·75	4·08	4·37	1·06	1·08
2	333·06	15·10	7·57	77·33	5·07	4·70	3·11	3·49	1·14	1·18
3	334·69	7·87	17·19	74·79	5·07	4·75	2·93	2·91	1·15	1·20
4	333·07	34·12	11·79	54·09	2·19	2·16	1·76	2·06	1·70	1·68
5	334·45	17·17	22·45	60·38	2·95	2·83	1·98	2·12	1·43	1·46
6	335·61	9·11	29·75	61·14	3·25	3·22	2·03	2·09	1·38	1·41
7	337·44	9·62	53·27	37·11	1·87	2·02	1·30	1·38	2·22	2·13
8	336·06	25·33	42·95	31·72	1·53	1·66	1·22	1·41	2·70	2·53

TABLE III.

Comparison of Experimental and Predicted Activity Coefficients.

System: Ethanol–methanol–water.

$$T \log \gamma_1 = \frac{72{\cdot}4x_2^2 + 58{\cdot}2x_2x_3}{(x_1 + 0{\cdot}862x_2 + 0{\cdot}51x_3)^2}$$

$$T \log \gamma_2 = \frac{44x_3^2 - 78{\cdot}2x_1x_3}{(x_2 + 1{\cdot}16x_1 + 0{\cdot}591x_3)^2}$$

$$T \log \gamma_3 = \frac{545x_1^2 + 213x_2^2 + 717x_1x_2}{(x_3 + 1{\cdot}96x_1 + 1{\cdot}69x_2)^2}$$

1 refers to ethanol.
2 refers to methanol.
3 refers to water.

Run No.	Temp., ° K.	Liquid composition (mol percentage).			Activity coefficients.					
					Ethanol.		Methanol.		Water.	
		Ethanol.	Methanol.	Water.	Predicted.	Expt.	Predicted.	Expt.	Predicted.	Expt.
39	340·9	20·0	77·5	2·5	1·01	0·98	0·99	0·97	1·80	1·41
4	342·8	6·4	68·3	25·3	1·18	1·10	1·01	1·03	1·46	1·08
13	344·2	3·6	62·5	33·9	1·28	1·44	1·04	1·04	1·36	1·03
15	346·7	27·4	41·5	31·3	1·16	1·11	0·98	1·02	1·55	1·24
1	350·9	51·7	10·6	37·7	1·14	1·10	0·94	1·04	1·65	1·48
10	350·9	64·1	6·3	29·6	1·07	1·05	0·93	0·98	1·83	1·73
25	351·6	19·3	19·7	61·0	1·63	1·58	1·08	1·24	1·23	1·00
11	353·6	28·6	6·1	65·3	1·59	1·64	1·05	1·36	1·24	1·03
28	356·1	14·2	5·2	80·6	2·50	2·58	1·30	1·67	1·08	0·87
32	356·7	7·5	9·2	83·3	3·00	3·58	1·45	1·57	1·05	0·81

TABLE IV.

Comparison of Experimental and Predicted Activity Coefficients.

System : *Iso*octane–toluene–phenol.

$T \log \gamma_1 = 41{\cdot}6x_2^2 + 434x_3^2 + 315{\cdot}6x_2x_3$
$T \log \gamma_2 = 41{\cdot}6x_1^2 + 160x_3^2 - 232{\cdot}4x_1x_3$
$T \log \gamma_3 = 434x_1^2 + 160x_2^2 + 552{\cdot}4x_1x_2$

1 refers to *iso*octane.
2 refers to toluene.
3 refers to phenol.

Run No.	Temp., °K.	Liquid composition (mol percentage).			Activity coefficients.					
					*Iso*octane.		Toluene.		Phenol.	
		Iso-octane.	Toluene.	Phenol.	Predicted.	Expt.	Predicted.	Expt.	Predicted.	Expt.
AA86	374·8	81·66	8·54	9·80	1·044	1·00	1·065	1·11	7·534	6·80
91	377·5	43·97	49·85	6·18	1·141	1·04	1·014	1·01	4·447	4·44
83	378·7	42·50	48·50	9·00	1·178	1·09	0·999	0·99	4·036	3·99
92	379·2	18·41	78·53	3·06	1·225	1·25	1·001	0·975	3·236	3·58
87	383·7	7·06	82·58	10·36	1·432	1·54	1·001	1·00	2·366	2·48
71	384·8	16·10	64·10	19·80	1·488	1·45	0·999	0·96	2·223	2·16
62	385·3	21·80	49·60	28·60	1·714	1·472	1·003	0·955	2·051	1·98
61	388·7	10·20	58·90	30·90	1·954	1·64	1·051	0·97	1·738	1·63
142	388·7	10·79	41·58	47·63	2·711	2·33	1·158	1·11	1·404	1·36
121	394·2	9·00	35·10	55·90	3·266	2·60	1·253	1·19	1·268	1·12
1	404·2	1·13	31·50	67·37	4·592	3·73	1·496	1·376	1·108	1·10
131	422·0	0·95	7·82	91·23	8·130	6·35	2·042	1·95	1·008	1·00

As for the system *n*-heptane–toluene–methanol, the relation presented by Equation (25), fortunately, actually holds.

The predicted ternary activity coefficients are compared with the observed values in Tables II to IV. The observed values are either read directly from the published article [6] or evaluated from the published equilibrium vapour–liquid compositions [1, 8] by means of the relation

$$\gamma_1 = \frac{Py_1}{p_1^0 x_1}.$$

In most cases, as shown in Tables II to IV, the predicted results are in good agreement with the experimental values, especially in the case of *n*-heptane in the system *n*-heptane–toluene–methanol where its activity coefficient (which represents the non-ideality) approaches eight.

b-RATIOS.

Of particular interest is the constant *b* which, as presented in the previously published equations equivalent to Equations (17) and (18), has been interpreted in different ways with different aspects. Van Laar [11] defined it as van der Waals' proper mole volume, and later Scatchard [13] defined it as the molar volume of a pure liquid. The evaluated results of the *b*-ratios given in Table I show neither to be the case.

As stated before, *b* is really the quantity of the partial molal volume, and, therefore, is a function of the composition of the mixture.[12] So, it cannot be expected to be a constant.

Different values of *b*-ratio have been obtained even when using the two

plots presented by Equations (17) and (18). From these two plots the b-ratio can be read in four different ways, namely

$$\frac{b_1}{b_2} = \left\{\frac{(\text{Intercept})_1}{(\text{Intercept})_1}\right\}^2 = \left(\frac{I_2}{I_1}\right)^2$$

$$\frac{b_1}{b_2} = \left\{\frac{(\text{Slope})_1}{(\text{Slope})_2}\right\}^{1/1.5} = \left(\frac{S_1}{S_2}\right)^{1/1.5}$$

$$\frac{b_1}{b_2} = \frac{(\text{Slope})_1}{(\text{Intercept})_1} = \frac{S_1}{I_1}$$

$$\frac{b_1}{b_2} = \frac{(\text{Intercept})_2}{(\text{Slope})_2} = \frac{I_2}{S_2}$$

Values of b-ratios for some binary systems read from the above relations are given in Table V.

TABLE V.

b-Ratios.

System.		b_1/b_2.			
Component 1.	Component 2.	$\left(\frac{I_2}{I_1}\right)^2$.	$\left(\frac{S_1}{S_2}\right)^{1/1.5}$.	$\frac{S_1}{I_1}$.	$\frac{I_2}{S_2}$.
n-Heptane	Toluene	1·15	1·69	1·57	1·50
n-Heptane	Methanol	1·15	1·17	1·26	1·07
Toluene	Methanol	1·00	1·00	1·00	1·00
Ethanol	Water	1·97	1·96	2·02	1·91
Methanol	Water	1·69	1·66	1·63	1·73
*Iso*octane	Toluene	1·00	1·00	1·42	0·71
*Iso*octane	Phenol	—	—	—	1·04
Toluene	Phenol	1·00	1·36	1·35	1·18

However, from personal experience, it has been found that any of the above values can be used in the ternary relations to predict activity coefficients without introducing great discrepancy.

So, for practical purpose, the b-ratios can be taken as constants. In the case of ternary systems, even when the b-ratios are not consistent with the relation indicated by Equation (25), they may still be used in ternary equations to predict activity coefficients.

SUMMARY.

Ternary vapour–liquid equilibria can be predicted by means of Equations (21) to (23) under the following conditions:—

1. The internal energy change in mixing varies directly with the collision frequency between molecules of different kinds.
2. The binary collision frequency between liquid molecules follows the relation indicated by Equation (5).
3. Change of partial molal volume with composition is slight.
4. The $\Delta(PV)$-change can be neglected in comparison with the internal energy change.

5. The entropy change on mixing for a solution where orienting and chemical effects are absent is the same as for an ideal solution.

6. The constant k is nearly independent of the presence of molecules other than those taking part in binary collisions. In other words the constant k in a ternary mixture will remain the same as it is in a binary mixture.

7. The data of binary systems should be restricted to a quantitative relation represented by Equation (25).

8. In the case of isobaric processes, an additional assumption is made that the constants k and b will remain unchanged over a short range of temperature.

List of Symbols.

C, C', C'' = Proportionality constant.
E = Internal energy.
ΔE = Internal energy change.
F = Free energy of a mixture.
F^0 = Free energy of a pure liquid.
$\bar{F}$ = Partial free energy.
ΔF = Free energy change.
ΔH = Enthalpy change.
I = Intercept.
P = Total pressure.
R = Gas constant.
ΔS = Entropy change.
S = Slope.
T = Boiling temperature, ° K.
V = Molar volume.
Z = Collision frequency.
a = Activity.
a = Proportionality constant.
b = Partial molal volume.
c = Number of molecules per unit volume.
d = Distance apart of centres on collision.
k = Boltzmann's constant.
k (with various subscripts) = Constant.
m = Mass of molecule.
n = Number of moles.
$\bar{n}$ = Number of moles per unit volume.
p = Partial pressure.
p^0 = Vapour pressure of a pure liquid.
x = Mol fraction in liquid phase.
y = Mol fraction in vapour phase.
z = Collision frequency per unit volume.
γ = Activity coefficient.

Subscripts.

A, B refer to components.
1, 2, ... i, . . . r refer to components.

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"TABLES FOR MEASUREMENT OF OIL"

Users of the above book should note the following corrigenda:

Arguments		Legend
sp. gr.	Temp.	should read
Table 11, *page* 57		
0·603	90	0·6195
Table 12, *page* 230		
0·605	96	0·9659
0·605	97	0·9649
0·605	98	0·9640
0·605	99	0·9630
0·605	100	0·9620